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PROJECT GASOLSYN

CONVERSION OF LIGHT ALCOHOLS TO HYDROCARBONS
OVER ZSM-5 ZEOLITE CATALYSTS

(FINAL REPORT SUBMITTED TO CANMET)

Raymond LE VAN MAO and Gerald P. McLAUGHLIN

(CANMET Scientific Authority: Dr. Gilles Jean)

Concordia University
Department of Chemistry
Catalysis Research Laboratory
1455 West, de Maisonneuve Boulevard
Montréal, Québec, CANADA

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SUMMARY OF THE MAIN CONCLUSIONS

As specified in the CANMET contract (Number 24St.23440-5-9095; Project Gasolsyn UP-C-616), the objective of the above mentioned research project is to test, under various reaction conditions, the following catalysts:

- pure ZSM-5 based catalyst (as reference catalyst);
- Zn-modified ZSM-5 zeolite catalyst;
- Zn-modified chryso-zeolite catalyst (chryso-zeolite = zeolite prepared from chrysotile asbestos).

The Zn-modified ZSM-5 zeolites and chryso-zeolites are now protected by several patents [US Patent 4,511,667 and CAN Patent 1,195,311 (1985); US Patent 4,615,995 (1986) and US Patent Application 875,191 (granted)] held by two Canadian agencies: the Canadian Patents Development Limited and the Canadian Asbestos Institute.

The alcohol feeds consisted of:

- methanol;
- n-butanol;
- iso-butanol;
- mixture of methanol, ethanol, propanol, and n-butanol. This mixture is a simulation of the products obtained from (hydrogen poor) synthesis gas, which can be derived from coal, according to the process developed by l'Institut Français du Pétrole.

With practically all the aforementioned alcohol feeds, both the Zn-modified zeolite or chryso-zeolite exhibited a much better catalytic performance than the parent ZSM-5 zeolite.

With pure methanol as feed, the following results were obtained (at 390 °C and 250 psi, i.e. under reaction conditions similar to those of the Mobil Methanol-To-Gasoline (MTG) process, except there was no gas recycling in our experiments, and at 470 °C and 100 psi):

CATALYSTS	REACTION CONDITIONS		MOST VALUABLE PRODUCTS YIELD (wt %)		CHARACTERISTICS OF THE LIQUID HYDROCARBONS		
	T (°C)	PRESSURE (psi)	C ₂ -C ₄ olefins	Liquid hydrocarbons	Aromatic content (wt %)	BTX content (wt %)	Durene content (wt %)
H-ZSM-5	390	250	3.1	24.9	44	12	16.6
Zn/ZSM-5	390	250	1.2	25.7	57	23	8.4
Zn/Chryso-Zeolite	390	250	8.1	23.2	43	15	8.8
H-ZSM-5	470	100	4.0	19.9	63	42	2.8
Zn/ZSM-5	470	100	6.8	23.3	59	43	2.6
Zn/Chryso-Zeolite	470	100	6.3	23.9	64	43	3.7

Thus, under the reaction conditions comparable to those of the MTG process, the incorporation of Zn in the ZSM-5 zeolite and chryso-zeolite decreased the production of durene practically by half.

The Zn / ZSM-5 showed a higher production of aromatic and BTX compounds, whereas the Zn / chryso-zeolite gave a higher yield in light olefins.

At higher temperature ($T = 470^{\circ}\text{C}$), the use of the Zn / chryso-zeolite ZSM-5 led to the following catalytic improvement:

- 70 % increase in the production of light olefins;
- 20 % increase in the production of liquid hydrocarbons. The characteristics of the liquid hydrocarbons, in terms of aromatic and BTX (benzene, toluene, ethylbenzene, and xylenes) contents were practically the same as with the parent ZSM-5 zeolite.

The best catalytic performance of the (Zn-modified) chryso-zeolite was obtained at temperatures higher than that used in the Mobil MTG process. However, at these temperatures, the (Zn-modified) chryso-zeolite ZSM-5 was much more stable than the parent ZSM-5 zeolite. We believe that under recycle conditions as used in the Mobil MTG plant in New-Zealand (the gas recycling permits a better control of the temperature in the catalyst bed and an increase in the production of liquid hydrocarbons by additional alkylation with the light olefins present in the recycle gas), the (Zn-modified) chryso-zeolite will result in higher yields in liquid hydrocarbons and higher aromatic contents.

Moreover, the following results were obtained using a $\text{C}_1 - \text{C}_4$ alcohol mixture ($T = 470^{\circ}\text{C}$ and $P = 100\text{ psi}$):

CATALYSTS	MOST VALUABLE PRODUCTS YEILD (wt %)		CHARACTERISTICS OF THE LIQUID HYDROCARBONS		
	C ₂ -C ₄ OLEFINS	LIQUID HYDROCARBONS	AROMATIC CONTENT (wt %)	B T X CONTENT (wt %)	DURENE CONTENT (wt %)
ZSM-5	12.2	23.8	55	39	0.6
Zn/ZSM-5	13.4	27.6	59	43	0.4
Zn/CHRYSO- ZEOLITE	13.9	25.5	62	47	0.4

According to the previous data, the use of our catalysts (in comparison with parent ZSM-5 zeolite catalyst) can:

- increase the production of liquid hydrocarbons by 10 to 15 wt %;
- increase the production of aromatics (in the liquid hydrocarbons) by 10 to 15 wt % as well as the BTX by 15 to 20 wt %.

Moreover, with the Zn-modified chryso-zeolite ZSM-5, there is an additional increase in the yield of light olefins (ethylene, propylene, and butenes) by 15 wt %.

- the formation of durene (one of the main problems of the Mobil process) was kept to very low values.

These results are of great interest to Canada for several reasons:

1. Canada is a country which is extremely rich in natural resources, such as coal, biomass, natural gas, and heavy oils. Synthesis gas may be derived from these raw materials. Methanol is currently produced in the Western provinces; however, hydrogen poor synthesis gas, which is generally obtained from coal, biomass, and heavy oils, can be turned into a mixture of light alcohols without the addition of hydrogen from other sources.

It is obvious that Canada is working towards the establishment of its own technology for deriving non-petroleum energy stocks and chemicals from the aforementioned natural resources. The economical - political - technological implications of such an objective is multiple and does not need to be emphasized.

The processes MTG and more broadly, light Alcohols-to-Gasoline / light olefins / aromatics are extremely interesting approaches.

2. To produce more gasoline with higher aromatic contents (octane boosters) represents a significant technological achievement in the energy field.

To produce more aromatics (mostly BTX aromatics) and more light olefins represents an important step ahead in the development of a technology for the production of non-petroleum derived "petrochemicals".

3. Chryso-zeolites produced from chrysotile asbestos do not have any environmental drawbacks. In fact, contrary to the parent

chrysotile asbestos fibers, the chryso-zeolites do not show any cytotoxic effects as recently evidenced in a series of tests made by a medical research team at the University of Sherbrooke.

The great activity and selectivity of the (Zn-modified) chryso-zeolite ZSM-5 constitute the first safe application of asbestos in the field of catalysis. This is a real positive signal to the asbestos industry of Québec and British Columbia.

Finally, if Canada were in position to set up its own technology "coal or biomass - synthesis gas - light alcohols - hydrocarbons", it would be worth taking into consideration the following aspects:

- instead of passing through the methanol stage, one can have the $C_1 - C_4$ alcohols route favored, provided that this process will be fully optimised;
- $C_1 - C_4$ alcohol mixtures will give more valuable products than methanol, particularly with catalysts developed by our research team.

INTRODUCTION

Canada is a country which is rich in natural resources, such as natural gas, coal, biomass, and heavy oils. Due to a rather unstable petroleum crude market, Canada has to seriously examine these resources and try to develop its own technology in order to eventually ensure its supplies in energy and chemical feedstocks. Apart from the classical Fischer - Tropsch technology, new routes passing through synthesis gas and then light alcohols are very attractive.

Since the development of a new process Methanol-To-Gasoline, or MTG, by Mobil Oil from the United States, and using a novel crystalline zeolite known as ZSM-5, there has been an upsurge in research to exploit related processes. Moreover, new catalysts, which permit the preparation of $C_1 - C_4$ alcohol mixtures from a relatively hydrogen poor synthesis gas, have been developed [A. Sugier and E. Freund, US Patent 4,122,110 (1978), Institut Français du Pétrole (IFP)]. It is worth mentioning that synthesis gas, obtained from biomass or coal, is poor in hydrogen, and if one wants to produce methanol from this synthesis gas, hydrogen from another source must be added.

In our laboratories, two new categories of ZSM-5 zeolite catalysts have been developed:

- chryso-zeolites prepared from chrysotile asbestos fibers (1, 2);
- Zn-modified ZSM-5 zeolites (3 - 5).

These two novel classes of zeolites were found to be extremely selective in the conversion of methanol to hydrocarbons, leading to high yields in aromatics and light olefins (3 - 6). Therefore, the main objective of this research project is to test the Zn-modified ZSM-5 zeolite and its chryso-zeolite counterpart, and compare their catalytic performances with that of the parent ZSM-5 zeolite. The feeds used in these experiments consisted of methanol, n-butanol, isobutanol, and a mixture of $C_1 - C_4$ alcohols (the latter is a simulation of the mixture obtained in the IFP process).

EXPERIMENTAL

I. PREPARATION OF THE CATALYSTS

For comparative purposes, the following three catalysts were prepared:

- HP-CAN10/Zn = a pure ZSM-5 zeolite in which Zn was incorporated by ion-exchange;
- HA-CAN9/Zn = a composite ZSM-5 zeolite / asbestos^(*) catalyst, in which Zn was incorporated by ion-exchange. The MLD (magnesium leaching degree) of the composite material was 97 %.
- HA-CAN12/Zn = a composite ZSM-5 zeolite / asbestos^(*) catalyst, in which Zn was incorporated by ion-exchange. The MLD of this sample was 92 %.

Two other samples were also prepared: HP-CAN10 (acid form of the pure ZSM-5 zeolite), used as reference sample, and HA-CAN9/Zn-Mn, the Zn and Mn bearing composite catalyst.

(*) also called chryso-zeolite ZSM-5 or ZSM-5 zeolite prepared from chrysotile asbestos fibers.

A. Preparation of the HP-CAN10 Sample

1. Synthesis of the ZSM-5 zeolite (See also 1, 2).

110 g of Silica Gel (Baker) (> 90 % silica by weight) were suspended in a solution prepared from 110 g of tetrapropylammonium bromide (Aldrich) and 7.0 g of NaOH dissolved in 300 ml of distilled water. The suspension was heated at

80 °C with vigorous stirring for 1 hour. Then, a solution of 11.5 g of sodium aluminate (Fisher, % by weight composition: $\text{Al}_2\text{O}_3 = 46.8$, $\text{Na}_2\text{O} = 28.4$, balance being water), dissolved in 90 ml of distilled water, was added. Heating was continued at 80 °C with vigorous stirring for 10 minutes. The suspension was transferred into a Hastelloy C-276 container, which was then put into a Parr autoclave, and heated for 10 days at 170 °C (± 5 °C). After cooling, the suspension was discharged and filtered; the solid was washed with distilled water until the washing liquid had a pH lower than 9, and then dried at 120 °C for 10 hours, and activated in the air at 550 °C for 12 hours (weight of the resulting solid: 107 g).

2. Ammonium ion-exchange

20 g of the solid previously obtained were brought in contact with an aqueous solution of ammonium chloride at 5 % weight, using 10 ml of solution per gram of compound. The suspension was heated at 80 °C under reflux condition and with moderate stirring. After 1 hour of heating, the suspension was allowed to settle, and the liquid was then rapidly removed. A fresh volume of ammonium chloride solution was added and the suspension was heated again for another hour. The same procedure was repeated several times, so that the entire operation lasted 5 hours. The suspension was filtered and the solid was washed until Cl^- ions were no longer present in the washings. The compound was dried at 120 °C for 12 hours and activated in the air at 550 °C for 12

hours. The resulting material (acid form or H-form) had the following chemical composition, as determined through atomic absorption (% by weight; dried oxides basis): $\text{SiO}_2 = 95.6$; $\text{Al}_2\text{O}_3 = 4.2$, and $\text{Na}_2\text{O} = 0.2$ (Si / Al molar ratio = 19). The degree of crystallinity, DC, determined according to the method of Le Van Mao et al (1), was 100 %.

3. Final catalyst form

The final catalyst was prepared according to the following procedure: the previously obtained solid was intimately mixed with bentonite (20 % by weight) and made into a paste with distilled water, 1 ml of water was used for each gram of the solid. The paste was pressed into 1 mm O.D. extrudates. Finally, the extrudates were dried at 120 °C for 12 hours and activated in the air at 550 °C for 12 hours. This sample was called HP-CAN10.

B. Preparation of the HP-CAN10/Zn Sample

1. Zn incorporation

The Zn loading onto the ZSM-5 (H-form or HP-CAN10) sample was done according to the following procedure: 13 g of the HP-CAN10 were brought in contact with an aqueous solution of ZnCl_2 (Mallinckrodt), at 1 % by weight, using 80 ml of solution. The suspension was heated at 80 °C under reflux and with moderate stirring. After 1 hour of heating, the suspension was cooled, then filtered and washed with distilled water, until Cl^- ions were no longer present in the

washings. The compound was dried at 120 °C for 12 hours and activated in the air at 550 °C for 12 hours. The Zn metal content was 0.51 % by weight.

2. Final catalyst form

The final catalyst was prepared by extrusion with bentonite, according to the procedure previously described. The resulting material was called HP-CAN10/Zn.

C. Preparation of the HA-CAN9/Zn

1. Preparation of the leached asbestos material (Alix 083)

The fibrous asbestos used in the present project was of type 7TF-12 chrysotile asbestos with short fibers. Its chemical composition, in % by weight, was: $\text{SiO}_2 = 42.8$, $\text{MgO} = 50.2$, $\text{Fe}_2\text{O}_3 = 6.6$ (under FeO and Fe_3O_4 forms), $\text{Al}_2\text{O}_3 = 0.1$, $\text{Na}_2\text{O} = 0.1$, and others = 0.2.

The Alix 083 used as precursor of the composite ZSM-5 zeolite / asbestos catalyst (HA-CAN9) was prepared by partially leaching the magnesium (and the iron) out of the asbestos materials by acid attack. 1200 g of chrysotile asbestos fibers (7TF-12 grade) were suspended in a solution prepared from 2.4 l of concentrated HCl and 9.6 l of distilled water.

The suspension was heated at 70 °C - 80 °C with rapid stirring for 4 hours. Then, 6 l of distilled water were added and the resulting suspension was allowed to stand for 12 hours at room temperature. The suspension was filtered

and washed with 6 l of distilled water at room temperature. The solid was dried at 120 °C for 12 hours (W = 519 g) and the chemical composition of the resulting material, called Alix 083, was, as follows (wt %): SiO₂ = 91.8, Al₂O₃ = 0.4, Na₂O = 0.1, MgO = 1.9, and Fe₂O₃ = 5.8. The magnesium leaching degree (MLD) of the Alix 083 was defined as:

$$(\text{MLD}) = \frac{(\text{MgO})_i - (\text{MgO})_f}{(\text{MgO})_i} \times 100 (\%)$$

where (MgO)_i and (MgO)_f were the magnesium contents (dried oxide basis) of the asbestos fibers and of the Alix 083, respectively. The MLD of the Alix 083 was = 96.2 %.

2. Synthesis of the zeolite component in the composite material

135 g of Alix 083 were suspended in a solution prepared from 110 g of tetrapropylammonium bromide (TPA Br, from Aldrich > 98 %), and 7 g of NaOH (Fisher) dissolved in 300 ml of distilled water. The suspension was heated at 70 °C - 80 °C for 1 hour under vigorous stirring. Then, a solution of 14 g of sodium aluminate (Fisher) in 90 ml of distilled water was added. Heating was continued at 70 °C - 80 °C with vigorous stirring for 10 minutes. The suspension was transferred into an Hastelloy C-276 container, which was then put into a Parr autoclave and heated at 170 °C (± 5 °C) for 10 days.

After cooling, the suspension was discharged and filtered; the solid was washed with distilled water until the washing liquid had a pH lower than 9 and then dried at 120 °C

for 12 hours and finally activated in the air at 550 °C for 12 hours. The resulting material, called A-CAN9 (W = 123 g), was the precursor for the catalyst HA-CAN9.

3. Ammonium ion-exchange

100 g of the A-CAN9 material were submitted to the ammonium ion-exchange following the procedure previously described. The resulting material (HA-CAN9 acid form or H-form) had the following chemical composition (% by weight, dried oxides basis): $\text{SiO}_2 = 91.1$, $\text{Al}_2\text{O}_3 = 3.8$, $\text{Na}_2\text{O} = 0.3$, $\text{MgO} = 1.6$, and $\text{Fe}_2\text{O}_3 = 3.2$. The molar Si / Al ratio was 20.2; MLD = 97 %; the degree of crystallinity (DC) was 100 %.

4. Zn incorporation

The Zn loading onto the HA-CAN9 was done according to the following procedure: 13 g of HA-CAN9 were brought in contact with an aqueous solution of ZnCl_2 (Mallinckrodt) at 1 % by weight, using 80 ml of solution. The suspension was heated at 80 °C under reflux and with moderate stirring. After 1 hour of heating, the suspension was cooled down, then filtered and washed with distilled water until Cl^- ions were no longer present in the washings. The compound was dried at 120 °C for 12 hours and activated in the air at 550 °C for 12 hours. The Zn metal content was 0.60 % by weight.

5. Final catalyst form

The final catalyst was prepared by extrusion with bentonite according to the procedure as previously described. The resulting material was called HA-CAN9/Zn.

D. Preparation of HA-CAN9/Zn-Mn

13 g of the HA-CAN9 powder (Section C.3) were brought in contact with an aqueous solution of ZnCl_2 at 1 % by weight, using 80 ml of solution. The suspension was heated at 80 °C under reflux and with moderate stirring. After 1 hour of heating, the suspension was cooled, then filtered and washed with distilled water until Cl^- ions were no longer present in the washings. The compound was dried at 120 °C for 12 hours and activated in the air at 550 °C for 12 hours. The Zn metal content was 0.40 wt %.

The previously obtained solid was intimately mixed with bentonite (20 % by weight) and made into a paste with an aqueous solution of MnCl_2 (6 % wt / wt of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 11 ml of solution were used for 13 g of the solid mixture. The paste was pressed into 1 mm O.D. extrudates. Finally, the extrudates were dried at 120 °C for 12 hours and activated in the air at 550 °C for 12 hours. This sample was called HA-CAN9/Zn-Mn and its Mn content was 1.28 wt %.

E. Preparation of the HA-CAN12/Zn

1. Preparation of the leached asbestos material (Alix 070)

600 g of chrysotile asbestos fibers (7TF-12 grade) were suspended in a solution prepared from 1.2 l of concentrated HCl and 4.8 l of distilled water. The suspension was heated at 70 °C - 80 °C with rapid stirring for 2 hours. Then, 3 l of distilled water were added and the resulting suspension was allowed to stand for 12 hours at room temperature. The

suspension was filtered and washed with 3 l of distilled water at room temperature. The solid was dried at 120 °C for 12 hours ($W = 271.5$ g) and the chemical composition of the resulting material, called Alix 070, was as follows (% by weight): $\text{SiO}_2 = 88.2$, $\text{Al}_2\text{O}_3 = 0.2$, $\text{Na}_2\text{O} = 0.1$, $\text{MgO} = 5.3$, $\text{Fe}_2\text{O}_3 = 6.2$. The MLD of the Alix 070 was 89.5 %.

2. Synthesis of the zeolite component in the composite material

67 g of Alix 070 were suspended in a solution prepared from 57 g of tetrapropylammonium bromide (Aldrich) and 3.6 g of NaOH (Fisher) dissolved in 156 ml of distilled water. The suspension was heated at 70 °C - 80 °C for 1 hour with vigorous stirring. Then, a solution of 6.7 g of sodium aluminate (Fisher) in 47 ml of distilled water was added. Heating was continued at 70 °C - 80 °C with vigorous stirring for 10 minutes. The suspension was transferred into an Hastelloy C-276 container, which was then put into a Parr autoclave and heated at 170 °C (± 5 °C) for 10 days. After cooling, the suspension was discharged and filtered; the solid was washed with distilled water until the washing liquid had a pH lower than 9 and then dried at 120 °C for 12 hours and finally activated in the air at 550 °C for 12 hours. The resulting material called A-CAN12 ($W = 57$ g) was the precursor for the catalyst HA-CAN12.

3. Ammonium ion-exchange

50 g of the A-CAN12 material were submitted to the ammonium ion-exchange following the procedure previously

described. The resulting material (HA-CAN12, acid form or H-form) had the following chemical composition (% by weight, dried oxides basis): $\text{SiO}_2 = 87.1$, $\text{Al}_2\text{O}_3 = 5.4$, $\text{Na}_2\text{O} = 0.3$, $\text{MgO} = 3.3$, and $\text{Fe}_2\text{O}_3 = 4.7$. The molar Si / Al ratio was 14; MLD = 93 %; degree of crystallinity (DC) = 100 %.

4. Zn incorporation

The Zn loading onto the HA-CAN12 was done according to the procedure previously described (See HP-CAN10/Zn and HA-CAN9/Zn). The Zn metal content of the HA-CAN12/Zn was 0.56 % by weight.

5. Final catalyst form

The final catalyst was prepared by extrusion with bentonite according to the procedure as previously described (see HP-CAN10).

II. CATALYTIC TESTING

A. Reaction Setting (See also FIGURE 1)

Alcohols are contained in a one litre Pyrex reservoir, the pumping of which is accomplished using a Milton Model Number 396-31 reciprocating mini-pump. The nitrogen used as a carrier gas is controlled by a Tescom Corporation Series 44-1100 pressure regulator, which maintains an inlet pressure 50 psi above the reaction pressure. The fine control of the flow rate is achieved via a micrometering valve and monitored using a gas transducer model Number 8143, by Matheson Gas Products Canada.

The alcohol and carrier gas are mixed in a heated zone prior to reaching the reaction vessel.

The reaction vessel is a single piece of 316 stainless steel with a volume of 103 ml divided into a pre-heating zone loaded with quartz beads supported on a stainless steel wire mesh, and a reaction zone with a fixed catalyst bed supported in a similar fashion. There is a stainless steel thermocouple well in the center of the reaction vessel where chromel-alumel thermocouples are inserted to monitor the temperatures of the various zones.

The entire reaction vessel is surrounded by a heating jacket, which is operated by a non-indicating, potentiometric, time-proportioning controller, the final temperature is controlled by a manual power input to each zone.

The desired pressure in the reaction vessel is maintained using a Tescom series 26-1700 back pressure regulator.

Gaseous and liquid products pass through a water cooled condenser then into a collecting flask immersed in an antifreeze solution, which is maintained at - 10 °C where the aqueous and organic liquids are trapped; the gas continues on through a dynamic gas sampling bulb, a second gas transducer connected to the M.F.M. and Totalizer and is then vented to a fumehood.

B. Product Characterization

The gaseous products were analyzed on-line by gas chromatography using 5 m long column packed with Chromosorb P coated with 20 % by weight of Squalane connected in series with a 2.5 m long

column packed with Carbopack graphite coated with picric acid (0.19 % by weight). 2,2-dimethylbutane was used as the internal standard. The GC used was a dual FID Hewlett-Packard Model 5790 equipped with a 3392A Model integrator. It was also equipped with a capillary column (length = 50 m; PONA type fused silica coated with a cross-linked polymer), which was used for routine analyses of the liquid fraction after a complete run. The composition of the aqueous layer was also determined by GC using a methanol in water calibration standard curve. For accurate analysis of the organic phase, a Hewlett-Packard GC/MSD (5970 Series Mass Selective Detector) was used.

C. Catalyst Testing Procedure

The five catalysts under study HA-CAN9/Zn, HP-CAN10/Zn, HA-CAN9/Zn-Mn, HP-CAN10, and HA-CAN12/Zn are all tested under the same reaction conditions. These conditions include three different pressures 50 psi, 100 psi, and 250 psi, as well as three different temperatures 390 °C, 430 °C, and 470 °C. Six grams of catalyst was used in each run, the alcohol is pumped at a rate of fifteen grams per hour and the nitrogen gas is maintained at 200 ml/min; these conditions give a WHSV of 2.5 hr⁻¹ and a N₂/alcohol of 1.0.

The reaction vessel, as previously described, consists of two zones, the preheating zone loaded with quartz beads is maintained at a temperature of 300 °C to heat the vaporized alcohol and prevent decomposition; the catalyst bed is maintained at the

reaction temperature. Reaction conditions are continuously monitored and recorded every twenty minutes.

The gas produced is analyzed by GC at eighty minutes intervals. The sampling is accomplished using a dynamic gas sampling bulb with a by-pass system, a sample of gas is sealed in the bulb, 1 μ l of the internal standard is injected and one hundred (100 μ l) is withdrawn and injected into the GC.

The organic and aqueous layers are collected in a cooled receiving flask, separated, weighted and analyzed by GC MSD and GC respectively.

D. Catalytic Tests

1. Catalysts

The four main samples HP-CAN10, HP-CAN10/Zn, HA-CAN9/Zn, and HA-CAN12/Zn were tested under the reaction conditions as mentioned below. Some catalytic runs were performed with the HA-CAN9/Zn-Mn sample.

2. Reaction temperatures and pressures

- Reaction temperatures = $T = 390\text{ }^{\circ}\text{C}$, $430\text{ }^{\circ}\text{C}$, and $470\text{ }^{\circ}\text{C}$.
- Pressures = $P = 50\text{ psi}$, 100 psi , and 250 psi .

3. Alcohol feeds

- a. Main feeds = methanol, n-butanol, and isobutanol.
- b. Mixture of linear $C_1 - C_4$ alcohols.

4. Other reaction parameters

- Nitrogen / alcohol molar ratio = 1
(nitrogen flow rate = 200 ml/min).

- WHSV (weight hourly space velocity) = 2.5 hr^{-1} .
- normal run duration = 7 hours.

5. Catalyst regeneration

Catalyst regeneration after a run was completed: heating in the air at 550°C for 12 hours.

RESULTS

Steady state

Reaction runs were performed for at least 7 hours. Under reaction conditions as described in the section EXPERIMENTAL, the steady state was usually reached after a few minutes under alcohol stream. The product distribution remained fairly constant during the reaction.

Data computation

Catalytic data collected were computed by means of a computer program which was run on an Olivetti M24 personal computer.

Two computing techniques were used to determine the total alcohol conversion, the conversion to hydrocarbons and the product selectivities:

1. direct determination of the product yields in the three (organic, aqueous, and gaseous) phases.

The yields in gaseous products were determined through the direct measurement of the flow-rate and the total amount of the gases at the outlet of the reactor after the condensing system.

2. direct determination of the product yields in the two liquid phases and indirect determination of the yields in the gaseous hydrocarbons based on the amount of water formed during the catalytic conversion of the alcohol.

Samples calculations are attached to this report. In most of the cases, the results obtained by both calculation techniques did not differ from each other by more than 3 %, i.e. within the experimental error margin commonly allowed.

The yields reported in this work were calculated on the basis of the indications from the various gas transducers connected to the reaction system. Since the transducers were not expected to give linear responses at all off-gas rates and the efficiency of the cooling system could be affected by high gas flow-rates, a complete recovery of the liquid and gaseous phases was practically impossible and a loss of the reaction products up to 3 wt % could easily occur.

Regarding the alcohol feed, the maximum theoretical yield (MTY) could be determined through the general formula:



- for methanol, the MTY amounts to 43.75 wt %;
- for n-butanol and isobutanol, the MTY amounts to 75.68 wt %;
- for the $C_1 - C_4$ alcohol mixture used in this work, the MTY amounts to 60.86 wt %.

A. Tests With Pure Methanol as Feed

1. Catalytic data obtained with the pure ZSM-5 zeolite based catalyst, the HP-CAN10 sample

TABLE 1 and FIGURE 2 report the catalytic data obtained with the HP-CAN10 (a ZSM-5 zeolite based catalyst) at 390 °C, 430 °C, and 470 °C as reaction temperatures, under 50 psi, 100 psi, and 250 psi total pressures.

In terms of liquid hydrocarbon yield ($C_5 - C_{11}$ hydrocarbons), the maximum values were observed at 100 psi circa, and this was the case for all three temperatures. The yield in

liquid hydrocarbons decreased as the temperature increased from 390 °C to 470 °C. The total aromatic and BTX aromatic (benzene, toluene, ethylbenzene, and xylenes) content increased with temperature. An increase in aromatic content with an increase in pressure at 390 °C and 430 °C was noted, while the reverse was seen with increasing pressure at 470 °C.

The BTX content itself always decreased with increasing pressure. The durene formation was rather high at lower temperature and higher pressure (for example, at 390 °C and 250 psi). C₂ - C₄ olefins were produced in relatively low yields. The loss in liquid hydrocarbon production when the reaction temperature was increased from 390 °C to 470 °C (under 100 psi pressure) was around 28 % while there was an increase in total aromatic content of 50 % and in BTX content of 110 %. It is worth mentioning that the ZSM-5 zeolite that we used had a Si/Al ratio of 20, which was the most efficient for the aromatization of the olefinic intermediates.

2. Catalytic data obtained with the Zn bearing ZSM-5 zeolite, the HP-CAN10/Zn sample

TABLE 2 and FIGURE 3 report the catalytic data obtained with the HP-CAN10/Zn at 390 °C, 430 °C, and 470 °C as reaction temperatures, under 50 psi, 100 psi, and 250 psi total pressures. In terms of liquid hydrocarbon yields, we observed similar results at 390 °C as with the HP-CAN10. However, the total aromatic and the BTX contents of the

liquid hydrocarbons produced by the Zn bearing catalyst were much higher (+ 29 % and + 55 % respectively). Moreover, the production of durene was sharply reduced.

At higher temperatures, there was a slight decrease in the liquid hydrocarbon yield (- 11 % at 470 °C). Increases in total aromatic and BTX contents were also observed with increasing temperatures (+ 5 % and + 39 %, respectively at 470 °C). Moreover, at 470 °C, the production of C₂ - C₄ olefins was nearly the double of that obtained with the pure zeolite based catalyst.

3. Catalyst data obtained with the composite ZSM-5 zeolite/asbestos catalyst, the HP-CAN9/Zn (higher MLD or lower Mg content)

TABLE 3 and FIGURE 4 report the catalytic data obtained with the composite catalyst, HA-CAN9/Zn, at 390 °C, 430 °C, and 470 °C as reaction temperatures, under 50 psi, 100 psi, and 250 psi total pressures.

The behavior of this catalyst was very similar to that of the HP-CAN10/Zn, except for the following situations:

- at 390 °C, the composite catalyst exhibited lower liquid hydrocarbon and aromatic yields.
- at 470 °C, the composite catalyst yielded more liquid hydrocarbons and light olefins, while the aromatic contents were nearly the same.

TABLE 4 and FIGURE 5 report the catalytic data of the composite catalyst HP-CAN9/Zn-Mn. The additional

incorporation of Mn significantly increased the yield in liquid hydrocarbons (+ 16 %), while the aromatic production was nearly the same.

4. Catalytic data with the composite ZSM-5 zeolite/asbestos catalyst, the HA-CAN12/Zn (lower MLD or higher Mg content)

TABLE 5 and FIGURE 6 report the catalytic data obtained with the composite catalyst, HA-CAN12/Zn, at 430 °C and 470 °C as reaction temperatures, under 50 psi, 100 psi, and 250 psi total pressures, as well as at 390 °C under 50 psi, 100 psi, 150 psi, 250 psi, and 350 psi total pressures.

It was observed that at 470 °C, the yields in liquid hydrocarbons were relatively high with very high total aromatic and BTX contents.

At 390 °C, the production of light olefins was high, while the yield in liquid hydrocarbons was kept at a decent level.

B. Tests With Pure n-Butanol as Feed

1. Catalytic data obtained with pure ZSM-5 zeolite based catalyst, the HP-CAN10 sample

TABLE 6 and FIGURE 7 report the catalytic data obtained with the HP-CAN10 at 390 °C and 470 °C as reaction temperatures, under 50 psi, 100 psi, and 250 psi total pressures, and at 430 °C under 100 psi total pressure.

In terms of yield in liquid hydrocarbons and their aromatic content, the maximum values were observed at 100 psi circa, and this was the case for all the three temperatures

tested. Actually, the yield of liquid hydrocarbons decreased as the temperature increased from 390 °C to 470 °C. However, the contents in total aromatic and BTX showed the opposite tendency. Moreover, the durene formation was surprisingly low in comparison with that observed with the runs performed in the presence of methanol.

2. Catalytic data obtained with the Zn bearing ZSM-5 zeolite, the HP-CAN10/Zn sample

TABLE 7 and FIGURE 8 report the catalytic data obtained with the HP-CAN10/Zn at 390 °C and 470 °C as reaction temperatures, under 50 psi, 100 psi, and 250 psi total pressures, and 430 °C under 100 psi total pressure.

The liquid hydrocarbon yield increased with increasing pressure and decreased with increasing temperature. The contents in total aromatics and BTX increased with increasing pressure and temperature. The production of durene was very low.

3. Catalytic data obtained with the Zn-modified chryso-zeolite ZSM-5, the HA-CAN12/Zn sample

TABLE 8 and FIGURE 9 report the catalytic data obtained with the HA-CAN12/Zn at 390 °C and 470 °C, as reaction temperatures under 50 psi, 100 psi, and 250 psi total pressures, and at 430 °C under 100 psi total pressure.

In terms of the total aromatic content in the liquid hydrocarbons, the maximum values were observed at 100 psi circa, and this was the case for all the three temperatures

studied. The yield of liquid hydrocarbons increased with increasing pressure, and decreased with increasing temperature. The contents of total aromatics and BTX increased with increasing temperature, whereas the formation of durene was kept at extremely low values.

FIGURES 10 and 11 show the variations in the contents of total aromatics and BTX to the reaction pressure ($T = 470^{\circ}\text{C}$). The Zn-modified chryso-zeolite (HA-CAN12/Zn) exhibited the highest values for the aforementioned aromatic characteristics.

C. Tests with pure iso-butanol as feed

1. Catalytic data obtained with the pure ZSM-5 zeolite based catalyst, the HP-CAN10 sample

TABLE 9 and FIGURE 12 report the catalytic data obtained with the HP-CAN10 at 390°C and 470°C , as reaction temperatures, under 50 psi, 100 psi, and 250 psi total pressures, and at 430°C under 100 psi total pressure.

The yield in liquid hydrocarbons increased with increasing pressure and decreased with increasing temperature. In terms of contents of total aromatics and BTX, the maximum values were observed at 100 psi circa, and increased with the temperature.

2. Catalytic data obtained with the Zn-bearing ZSM-5 zeolite, the HP-CAN10/Zn sample

TABLE 10 and FIGURE 13 report the catalytic data obtained with the HP-CAN10/Zn at 390°C , 430°C , and 470°C , as reaction temperatures, under 50 psi, 100 psi, and 250 psi total pressures.

The yield of liquid hydrocarbon increased with increasing pressure and decreased with increasing temperature. The contents of total aromatics and BTX increased with the temperature. Again, the durene formation was very low.

3. Catalytic data obtained with the Zn-modified chryso-zeolite ZSM-5, the HA-CAN12/Zn sample

Similar trends were observed (TABLE 11 and FIGURE 14) as with the HP-CAN10/Zn.

Finally, FIGURE 15 shows the remarkable catalytic performance of the chryso-zeolite with respect to the two other catalysts.

D. Tests with a mixture of linear light alcohols as feed

A mixture of light alcohols was prepared according to the indications of the catalytic process developed by l'Institut Français du Pétrole (IFP). The composition of such a mixture was follows: methanol = 24.1 wt %, ethanol = 39.7 %, propanol = 21.9 wt %, and n-butanol = 14.3 wt %.

TABLE 12 reports the catalytic data obtained with this light alcohol mixture over the three catalysts studied.

The best catalyst, in terms of yield of liquid hydrocarbons and light olefins, and also contents of total aromatics and BTX, was the Zn-modified chryso-zeolite ZSM-5, the HA-CAN12/Zn.

GENERAL DISCUSSION ON THE CATALYTIC RESULTS

TABLE 13 reports the catalytic data of the most representative performances of our catalysts with respect to the pure ZSM-5 zeolite based sample (HP-CAN10), in the presence of pure methanol as feed.

The catalytic data at 390 °C of the HP-CAN10, which served as a reference sample, was very close to that of the Mobil's catalysts, which were tested under similar reaction conditions. As the temperature went up to 470 °C, a sharp decrease in liquid hydrocarbon production (- 28 %) was observed, while the total aromatic and BTX yields increased significantly.

With the Zn bearing ZSM-5 zeolite catalyst (HP-CAN10/Zn), such a decrease (in liquid hydrocarbon yield) with increasing temperature was much less (- 11 %). However, with respect to the catalytic data of the HP-CAN10 at 390 °C, there were important increases in aromatic and BTX yields (+ 17 % and + 44 % at 390 °C; + 18 % and + 17 % at 470 °C, respectively).

With the composite catalysts, the best catalytic performances were observed at 430 °C and 470 °C. At these temperatures, the production of liquid hydrocarbons was fairly high and constant (versus the temperature or pressure changes). On the other hand, the yields in total aromatics and BTX were unexpectedly high.

Comparing the catalytic performance of the HP-CAN10/Zn and the HA-CAN12/Zn with the performance of the reference sample, the HP-CAN10, we can see the following differences depending on the reaction temperature of the latter sample:

- HP-CAN10/Zn versus HP-CAN10 at 390 °C and 250 psi (MTG process):

- . Liquid hydrocarbons = + 3.2 %
- . Total aromatics = +30 %
- . BTX aromatics = + 92 %
- . Light olefins = - 61 %
- . Durene = - 49 %

FIGURE 16 shows the variations of the durene content in the liquid hydrocarbons in the liquid hydrocarbons at 390 °C observed with the HP-CAN10, HP-CAN10/Zn, and HA-CAN12/Zn. FIGURES 17 to 19 report the aromatic product distribution observed with the aforementioned catalysts.

- HA-CAN12/Zn versus HP-CAN10 at 470 °C and 100 psi:

- . Liquid hydrocarbons = + 20 %
- . Total aromatics = + 23 %
- . BTX aromatics = + 29 %
- . Light olefins = + 83 %
- . Durene = - 14 %

Thus, it seems to be very advantageous to use the composite catalysts which work better at higher temperatures to produce: more aromatics and BTX, less durene and much more C₂ - C₄ olefins, however, some limited loss in the liquid hydrocarbon yield is expected.

Now, let us figure out the situation where our difference catalysts are used in the Mobil's MTG process as in operation in New-Zealand.

FIGURE 20 shows the scheme (very simplified) of such an industrial plant. Methanol is first converted to a mixture of dimethylether and water, over an alumina catalyst (Reactor I). The mixture obtained is then mixed with recycle gases (rich in $C_1 - C_4$ hydrocarbons) in a 9:1 volume ratio (9 for the recycle gases: this high recycle ratio value ensures a better heat control and a higher liquid hydrocarbon yield). The resulting gaseous mixture now passes through a ZSM-5 zeolite bed contained in the Reactor II, which is usually set at 375 °C (average value) and 200 - 250 psi. A part of the gaseous hydrocarbons (practically the same quantity of gases produced by the feed methanol) is sent to the alkylation reactor (Reactor III, which contains sulfuric acid or HF as catalyst). The $C_2 - C_4$ olefins over a very acidic catalyst react with $C_2 - C_4$ paraffins (mostly with isobutane, which is produced to a very large extent by the ZSM-5 catalyst) to yield alkylates, which are then sent to the gasoline pool. However, this operation is not necessary if Reactor II is working in the most efficient way (i.e. high gas recycle ratio and high W.H.S.V.). Thus, the production of the liquid hydrocarbons (gasoline) can reach a 75 - 85 wt % with respect to the maximum theoretical yield of methanol (i.e. 32.8 - 37.2 wt % versus 43.75 wt % as maximum theoretical yield).

In TABLE 13 (the last 4 columns), we try to predict the maximum liquid yield if our catalysts were used in the MTG plant (obviously, the Reactor II must be set under reaction conditions as close as possible to those described in the present report).

The predicted maximum yield is defined as follows:

(yield in liquid hydrocarbons [A]) + (yield in $C_2 - C_4$ olefins [D]) + (equivalent amount of $C_2 - C_4$ paraffins)

Let us consider the HP-CAN10 (pure ZSM-5 based) catalyst, which is supposed to be working at 390 °C; its maximum gasoline yield would be 85 % and this value is very close to the data obtained by Mobil Oil with its fixed bed technology [activity of this sample at 470 °C (72 %) was too low to be taken into account although the aromatic content was rather interesting]. The aromatic and BTX contents in the final gasoline would be 30 % and 15 %, respectively and the durene content would be 5.3 %.

With all our composite catalysts working at 430 °C and 470 °C, the maximum gasoline yield would be much higher (around 90 %), and the total aromatic and BTX contents would have the following values: 38 and 26 % respectively, with a durene content of 2.2 % (case of the HA-CAN12/Zn at 470 °C).

In the presence of n-butanol and isobutanol, the production of total aromatics and BTX was extremely high over the three catalysts studied. The durene formation was kept at a very low level. Similar trends were observed with the linear alcohol mixture (TABLE 12). The highest catalytic performance was shown by the Zn-modified chryso-zeolite ZSM-5.

GENERAL CONCLUSION

In the presence of methanol as feed, Zn-modified zeolites or chryso-zeolites have shown their superiority over the parent ZSM-5 zeolite for the production of liquid hydrocarbons and high octane rating aromatics. The incorporation of Zn into the ZSM-5 lattice by ion-exchange has also contributed to a significant decrease in the formation of durene. Durene (1,2,4,5-tetramethylbenzene) has the unfortunate tendency of crystallizing out of the gasoline at low ambient temperature when the concentration exceeds 4 - 5 wt %. Since the market for durene is very limited, a low production of durene as reaction side-product also means a significant technological advantage for any "alcohol-to-hydrocarbons" process.

The use of higher alcohols as feed has led to increased yields of aromatics and surprisingly extremely low durene formation.

These positive trends were also observed with the light alcohol mixture which simulated the product stream from a novel process being presented as an alternative of the methanol synthesis.

Therefore, the fairly higher catalytic performance of our catalysts with respect to the parent ZSM-5 zeolite makes them candidates for any alcohol based technology aimed at producing high grade gasolines or chemical building blocks (light olefins and aromatics).

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REACTION CONDITIONS		PRODUCT YIELD (g/100g alcohol injected)				GASOLINE CHARACTERISTICS			
Temp C	Press. p.s.i.	C ₁ -C ₄ paraffins	C ₂ -C ₄ olefins	C ₅ -C ₁₁ liquid(gasoline)	Aromatic (wt%)	BTX (wt%)	Durene (wt%)		
390	50	10.7	6.9	24.4	39	22	4.6		
	100	11.5	3.9	27.6	42	20	7.1		
	250	13.8	3.1	24.9	44	12	16.6		
430	50	11.8	6.3	24.4	49	31	3.2		
	100	13.5	4.0	25.9	47	27	4.6		
	250	14.1	3.2	24.5	50	20	10.7		
470	50	16.4	5.7	19.2	61	41	2.0		
	100	18.2	4.0	19.9	63	42	2.8		
	250	17.2	2.8	19.5	57	31	5.0		

TABLE 1. CATALYTIC DATA FOR HP-CAN 10 WITH PURE METHANOL

REACTION CONDITIONS		PRODUCT YIELD (g/100g alcohol injected)				GASOLINE CHARACTERISTICS			
Temp C	Press. p.s.i.	C ₁ -C ₄ paraffins	C ₂ -C ₄ olefins	C ₅ -C ₁₁ liquid(gasoline)	Aromatic (wt%)	BTX (wt%)	Durene (wt%)		
390	50	12.9	5.7	25.4	45	30	3.4		
	100	18.3	1.6	26.2	54	31	6.0		
	250	17.5	1.2	25.7	57	23	8.4		
430	50	11.7	6.9	23.3	54	37	2.6		
	100	12.8	4.8	24.8	50	33	3.6		
	250	11.9	2.2	25.3	52	21	9.4		
470	50	9.6	11.7	20.6	56	43	1.4		
	100	12.7	6.8	23.3	59	43	2.6		
	250	14.7	4.4	22.1	52	29	5.7		

TABLE 2 CATALYTIC DATA F. R. HP-CAN 10/Zn WITH PURE METHANOL FEED

REACTION CONDITIONS		PRODUCT YIELD (g/100g alcohol injected)				GASOLINE CHARACTERISTICS			
Temp C	Press. p.s.i.	C ₁ -C ₄ paraffins	C ₂ -C ₄ olefins	C ₅ -C ₁₁ liquid(gasoline)	Aromatic (wt%)	BTX (wt%)	Durene (wt%)		
390	50	9.8	12.7	18.4	22	11	1.7		
	100	10.5	8.2	24.4	40	18	7.2		
	250	11.5	5.3	24.6	41	15	11.5		
430	50	8.9	10.0	23.6	52	38	2.0		
	100	9.3	9.2	23.1	47	28	4.4		
	250	13.8	3.8	25.5	52	27	6.9		
470	50	7.2	12.4	21.4	59	42	2.1		
	100	9.5	8.8	23.6	59	40	3.2		
	250	14.3	4.7	24.1	54	32	5.7		

TABLE 3 CATALYTIC DATA FOR HA-CAN 9/Zn WITH PURE METHANOL FEED

REACTION CONDITIONS		PRODUCT YIELD (g/100g alcohol injected)				GASOLINE CHARACTERISTICS			
Temp C	Press. p.s.i.	C ₁ -C ₄ paraffins	C ₂ -C ₄ olefins	C ₅ -C ₁₁ liquid(gasoline)	Aromatic (wt%)	BTX (wt%)	Durene (wt%)		
390	50	8.5	13.8	20.4	42	23	2.1		
	100	10.0	11.0	21.9	43	20	3.9		
	150	10.7	9.2	23.2	45	20	5.6		
	250	10.5	8.1	23.2	43	15	8.8		
	350	10.7	7.7	23.4	46	13	14.0		
430	50	9.5	10.7	23.1	46	36	1.5		
	100	10.6	8.4	22.5	46	30	3.2		
	250	13.3	4.0	24.8	46	24	7.0		
470	50	9.1	11.4	20.9	57	45	1.4		
	100	12.0	6.3	23.9	64	43	3.7		
	250	15.7	3.8	22.7	62	36	6.4		

TABLE 5 CATALYTIC DATA FOR HA-CAN 12/Zn WITH PURE METHANOL

REACTION CONDITIONS		PRODUCT YIELD (g/100g alcohol injected)				GASOLINE CHARACTERISTICS			
Temp C	Press. p.s.i.	C ₁ -C ₄ paraffins	C ₂ -C ₄ olefins	C ₅ -C ₁₁ liquid(gasoline)	Aromatic (wt%)	BTX (wt%)	Durene (wt%)		
390	50	15.4	12.3	40.6	30.1	23.4	0.2		
	100	18.0	7.8	43.6	32.0	23.2	0.3		
	250	16.0	4.7	43.0	32.5	22.4	0.3		
430	100	24.8	7.9	36.0	45.7	37.9	0.1		
470	50	19.4	21.1	28.7	46.0	39.1	0.1		
	100	26.4	10.3	32.5	57.1	48.6	0.1		
	250	25.4	5.4	33.2	56.3	45.3	0.2		

TABLE 6 CATALYTIC DATA FOR HP-CAN 10 WITH PURE n-BUTANOL AS FEED

REACTION CONDITIONS		PRODUCT YIELD (g/100g alcohol injected)				GASOLINE CHARACTERISTICS			
Temp C	Press. p.s.i.	C ₁ -C ₄ paraffins	C ₂ -C ₄ olefins	C ₅ -C ₁₁ liquid(gasoline)	Aromatic (wt%)	BTX (wt%)	Durene (wt%)		
390	50	15.9	16.3	37.1	31.9	24.6	0.2		
	100	17.5	9.8	40.9	34.7	25.7	0.2		
	250	20.1	6.0	41.9	37.7	27.3	0.3		
430	100	20.9	8.6	38.8	44.2	35.7	0.2		
470	50	17.5	18.0	31.5	51.9	46.2	0.1		
	100	21.3	9.6	34.7	57.1	49.0	0.1		
	250	24.4	4.8	35.2	60.6	49.4	0.1		

TABLE 7 CATALYTIC DATA FOR HP-CAN 10/Zn WITH PURE BUTANOL

REACTION CONDITIONS		PRODUCT YIELD (g/100g alcohol injected)				GASOLINE CHARACTERISTICS			
Temp C	Press. p.s.i.	C ₁ -C ₄ paraffins	C ₂ -C ₄ olefins	C ₅ -C ₁₁ liquid(gasoline)	Aromatic (wt%)	BTX (wt%)	Durene (wt%)		
390	50	13.6	15.3	39.9	27.8	21.0	0.2		
	100	12.0	9.0	44.7	28.8	20.8	0.2		
	250	12.8	7.7	47.4	26.5	17.0	0.3		
430	100	20.9	9.3	39.6	46.4	38.6	0.2		
470	50	20.1	17.4	30.7	57.8	52.4	0.1		
	100	21.9	9.9	35.2	60.7	53.3	0.1		
	250	26.0	6.7	35.9	58.1	48.1	0.2		

TABLE 8 CATALYTIC DATA FOR HA-CAN 12/Zn WITH PURE n-BUTANOL AS FEED

REACTION CONDITIONS		PRODUCT YIELD (g/100g alcohol injected)				GASOLINE CHARACTERISTICS			
Temp C	Press. p.s.i.	C ₁ -C ₄ paraffins	C ₂ -C ₄ olefins	C ₅ -C ₁₁ liquid(gasoline)	Aromatic (wt%)	BTX (wt%)	Durene (wt%)		
390	50	19.7	10.6	37.4	44.2	28.6	0.2		
	100	20.7	7.1	41.5	45.9	28.9	0.2		
	250	19.8	6.3	43.6	41.0	23.2	0.3		
430	100	22.2	9.1	36.7	51.7	35.0	0.2		
470	50	22.2	17.9	28.7	57.4	45.0	0.1		
	100	27.5	8.1	31.1	67.9	52.2	0.1		
	250	26.9	6.0	34.1	63.9	45.6	0.1		

TABLE 9 CATALYTIC DATA FOR HP-CAN 10 WITH PURE ISO-BUTANOL AS FEED

REACTION CONDITIONS		PRODUCT YIELD (g/100g alcohol injected)				GASOLINE CHARACTERISTICS			
Temp C	Press. p.s.i.	C ₁ -C ₄ paraffins	C ₂ -C ₄ olefins	C ₅ -C ₁₁ liquid(gasoline)	Aromatic (wt%)	BTX (wt%)	Durene (wt%)		
390	50	10.8	18.7	42.8	23.5	13.3	0.2		
	100	13.3	12.6	43.6	30.9	16.6	0.3		
	250	14.0	8.7	46.6	32.3	15.3	0.3		
430	100	19.1	12.0	38.4	43.5	29.7	0.2		
470	50	18.2	20.5	31.0	52.6	42.5	0.1		
	100	21.5	12.7	34.2	56.6	43.4	0.1		
	250	23.2	9.2	36.0	58.6	41.3	0.2		

TABLE 10. CATALYTIC DATA FOR HP CAN 10/Zn WITH PURE ISO-BUTANOL AS FEED

REACTION CONDITIONS		PRODUCT YIELD (g/100g alcohol injected)				GASOLINE CHARACTERISTICS			
Temp C	Press. p.s.i.	C ₁ -C ₄ paraffins	C ₂ -C ₄ olefins	C ₅ -C ₁₁ liquid(gasoline)	Aromatic (wt%)	BTX (wt%)	Durene (wt%)		
390	50	14.1	17.1	38.8	31.9	20.0	0.1		
	100	15.8	12.2	43.8	34.9	20.3	0.2		
	250	15.2	7.2	43.0	38.2	20.7	0.3		
430	100	20.2	11.2	37.5	50.4	36.0	0.2		
470	50	17.8	19.9	29.2	61.5	51.4	0.1		
	100	20.8	11.5	32.6	62.0	49.7	0.1		
	250	23.3	7.0	35.2	64.8	49.3	0.1		

TABLE 11 CATALYTIC DATA FOR HA-CAN 12/Zn WITH PURE ISO-BUTANOL AS FEED

CATALYST	REACTION TEMP °C (1)	PRODUCT YIELDS (wt%) (2)				PREDICTED YIELDS (3)				
		liquid hydrocarbons [A]	Total Aromatics [B]	BTX Aromatics [C]	C ₂ -C ₄ Olefins [D]	Maximum Gasoline (4)	% vs. Theoretical yield	Total Aromatic Content	BTX Content	
HP-CAN 10	390	27.6	11.3	5.5	4.7	37.0	85	30	15	
HP-CAN 10	430	25.9	12.4	7.3	4.0	33.9	77	37	21	
HP-CAN 10	470	19.9	12.1	8.0	4.3	28.5	65	42	28	
HP-CAN10/Zn	390	26.2	13.2	7.9	2.7	31.6	72	42	25	
HP-CAN10/Zn	470	23.3	13.3	9.4	8.4	40.1	92	33	23	
HA-CAN9/Zn	430	23.7	11.9	7.8	9.4	42.5	97	28	18	
HA-CAN9/Zn-Mn	430	26.8	13.2	8.6	7.1	41.0	94	32	21	
HA-CAN9/Zn	470	23.6	13.9	9.5	9.7	43.0	98	32	22	
HA-CAN12/Zn	470	23.9	14.8	10.3	7.9	39.7	91	38	26	

(1) Other reaction conditions Pe100psi, nitrogen/alcohol=1, WHSV=2.5hr⁻¹

(2) Mean values as determined through the graphs of Figures 1-5

(3) and (4) See explanations in section "Results and Discussion"

TABLE 13 Comparison of the product distributions from the best performing catalysts in the presence of methanol as feed

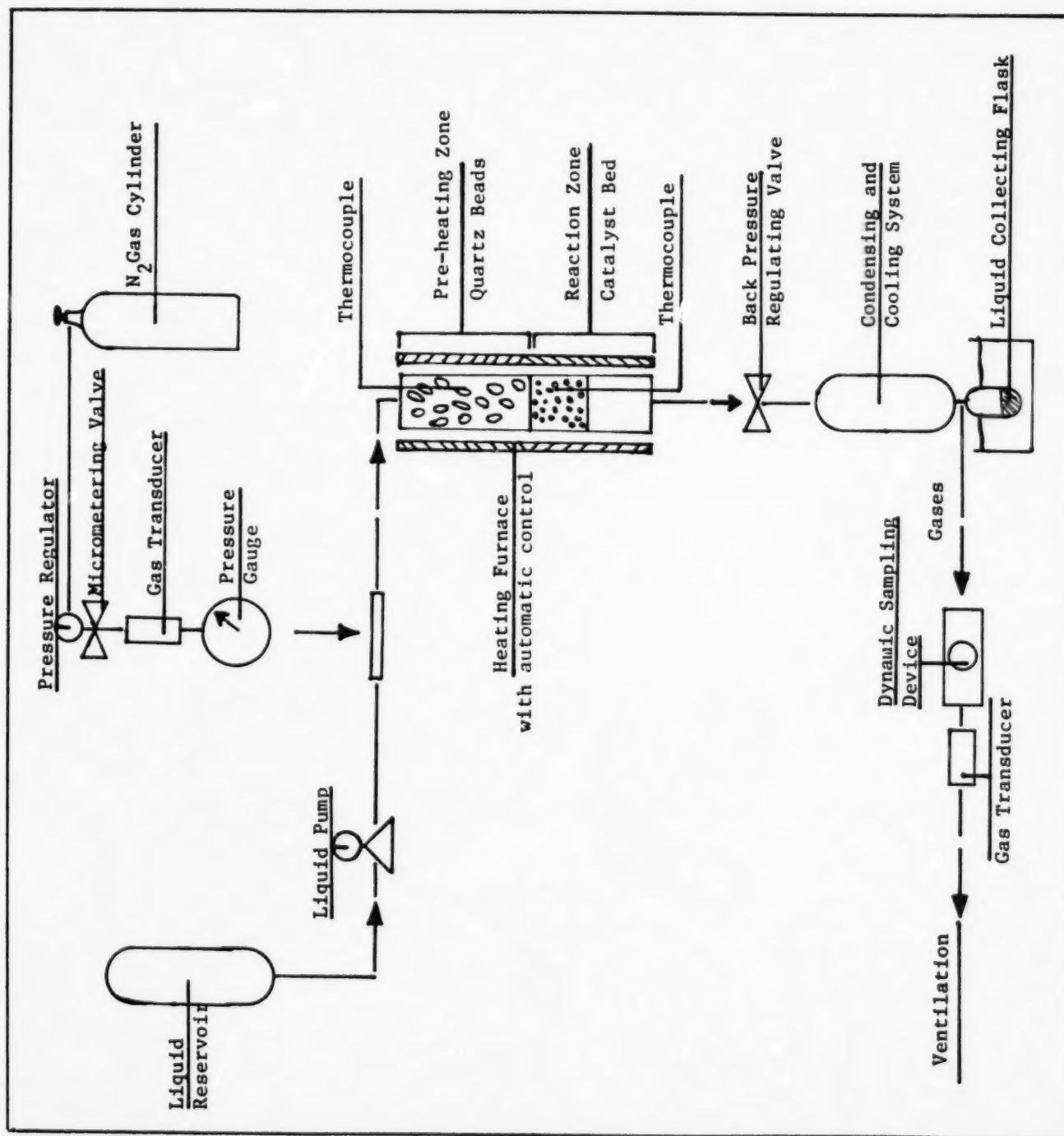


FIGURE 1: Catalytic Reaction Setting

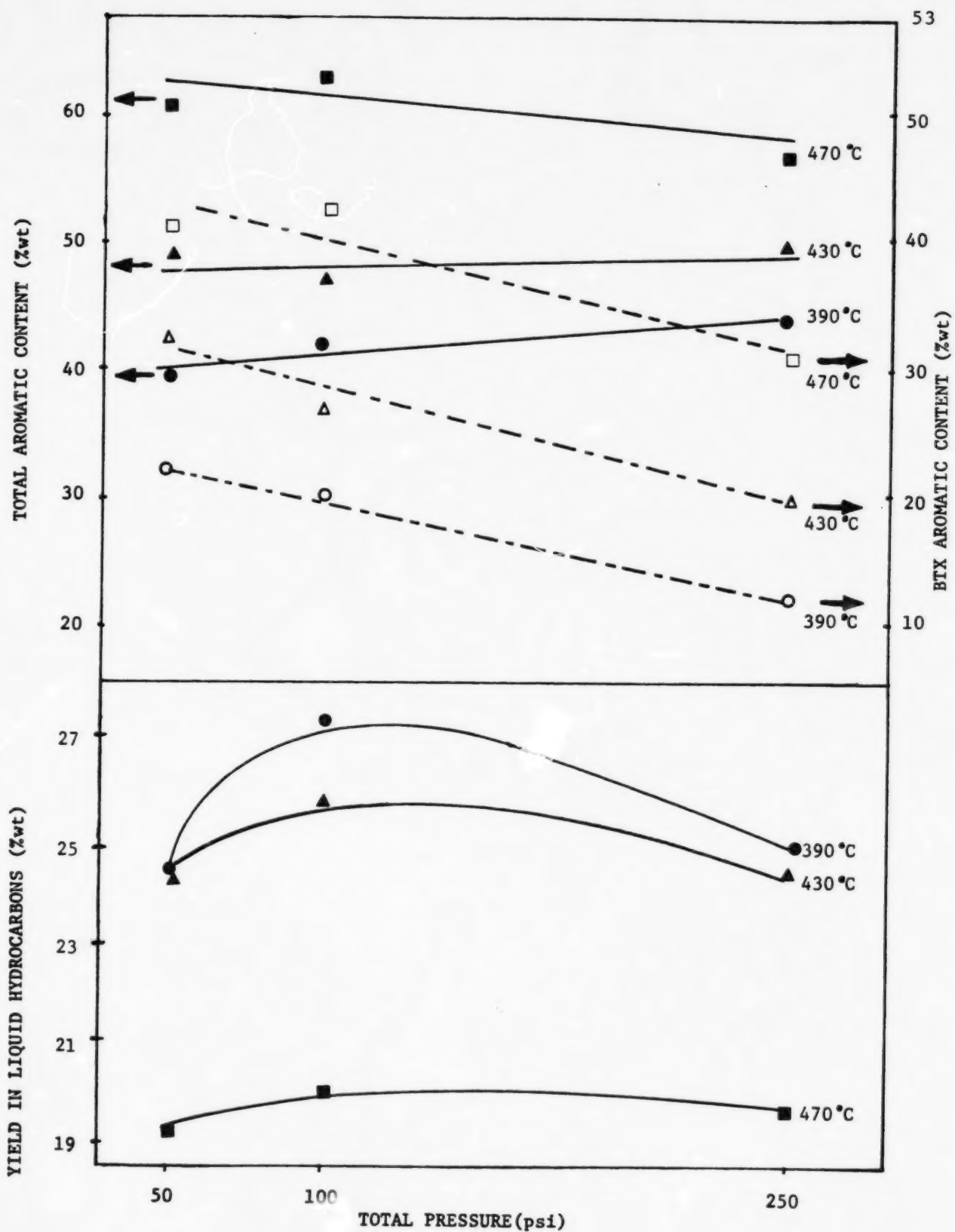


FIGURE 2: CATALYTIC BEHAVIOR OF HP-CAN 10 WITH PURE METHANOL

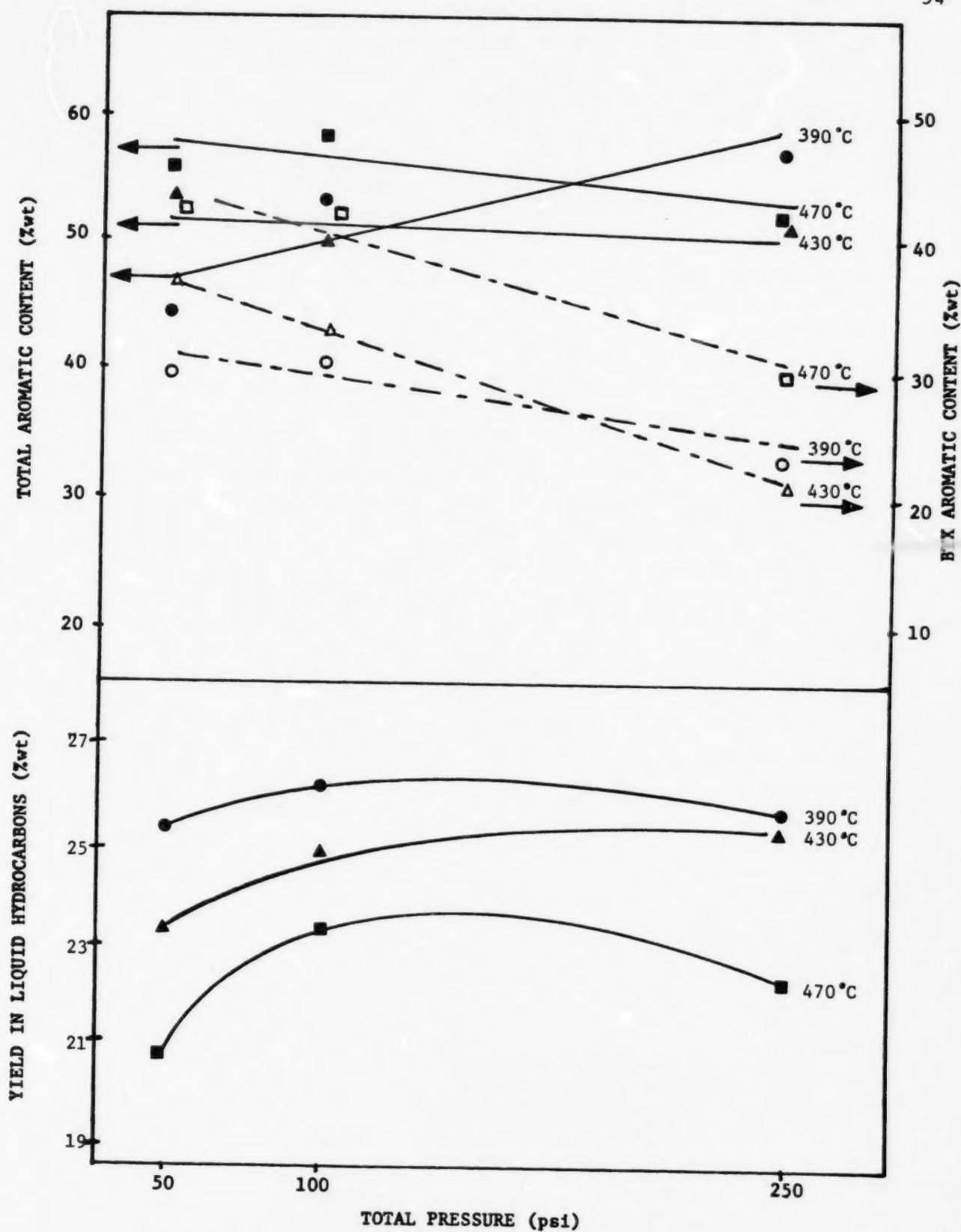


FIGURE 3: CATALYTIC BEHAVIOR OF HP-CAN10/Zn WITH PURE METHANOL

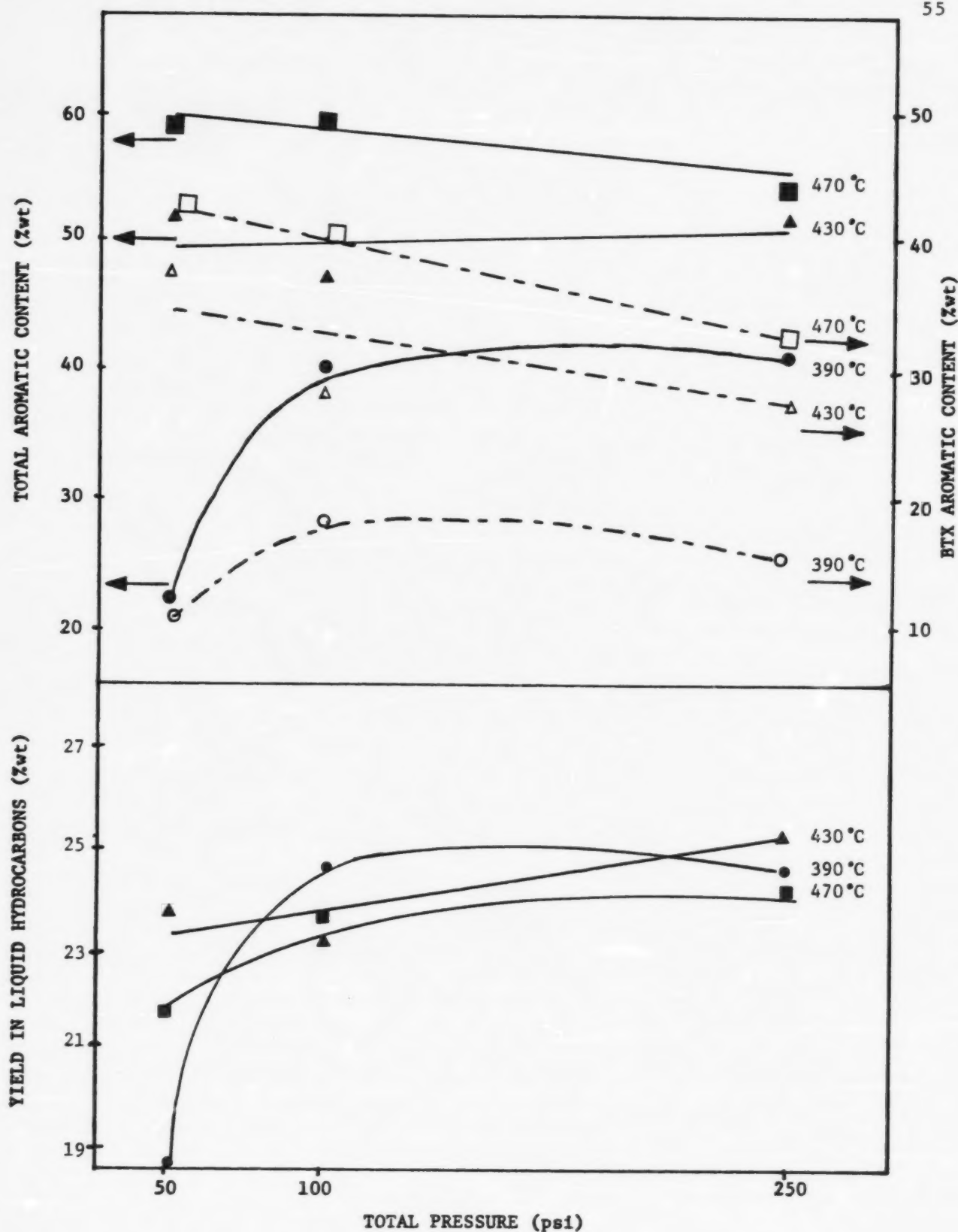


FIGURE 4: CATALYTIC BEHAVIOR OF HA-CAN 9/Zn WITH PURE METHANOL

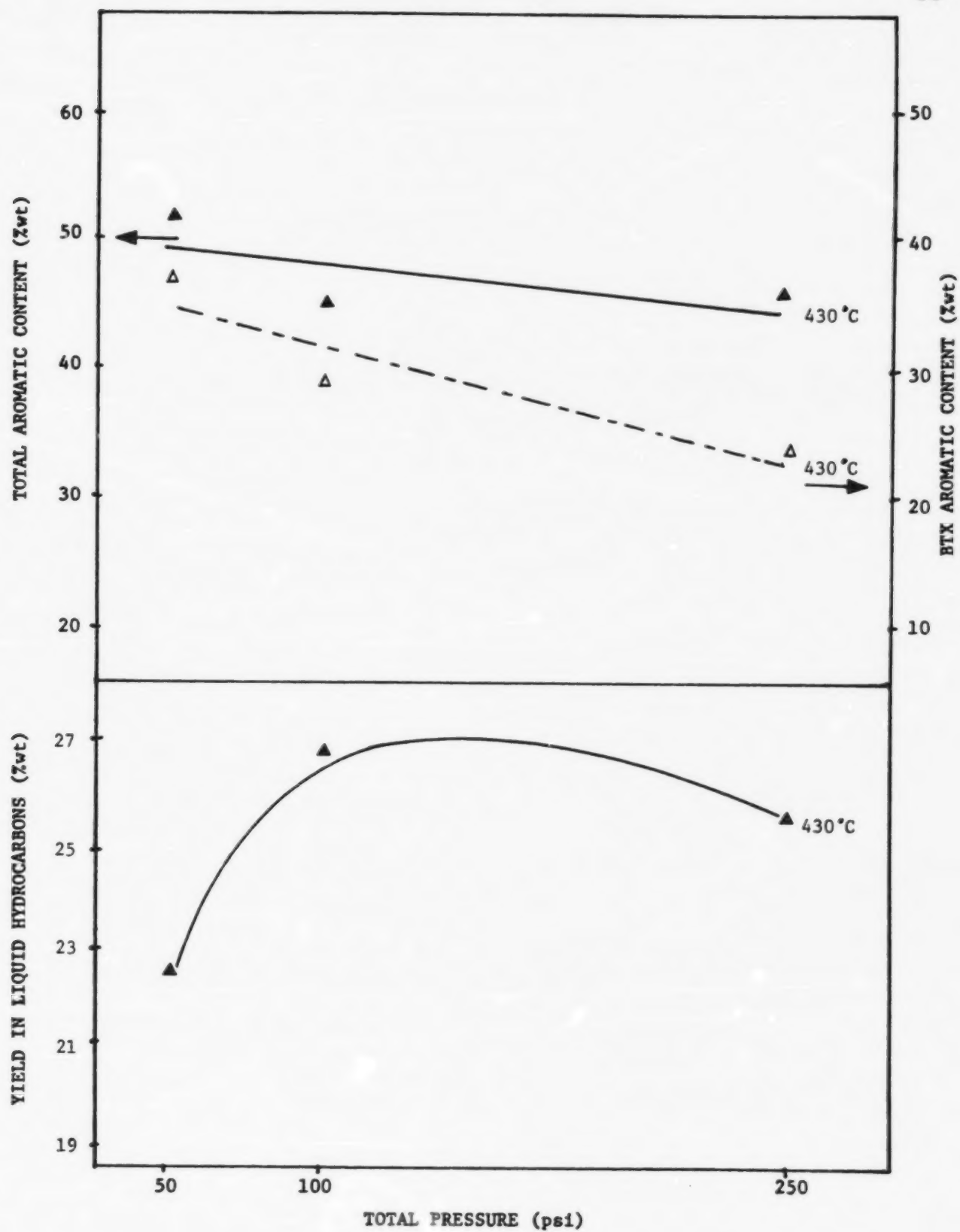


FIGURE 5: CATALYTIC BEHAVIOR OF HA-CAN 9/Zn₂-Mn₁ WITH PURE METHANOL

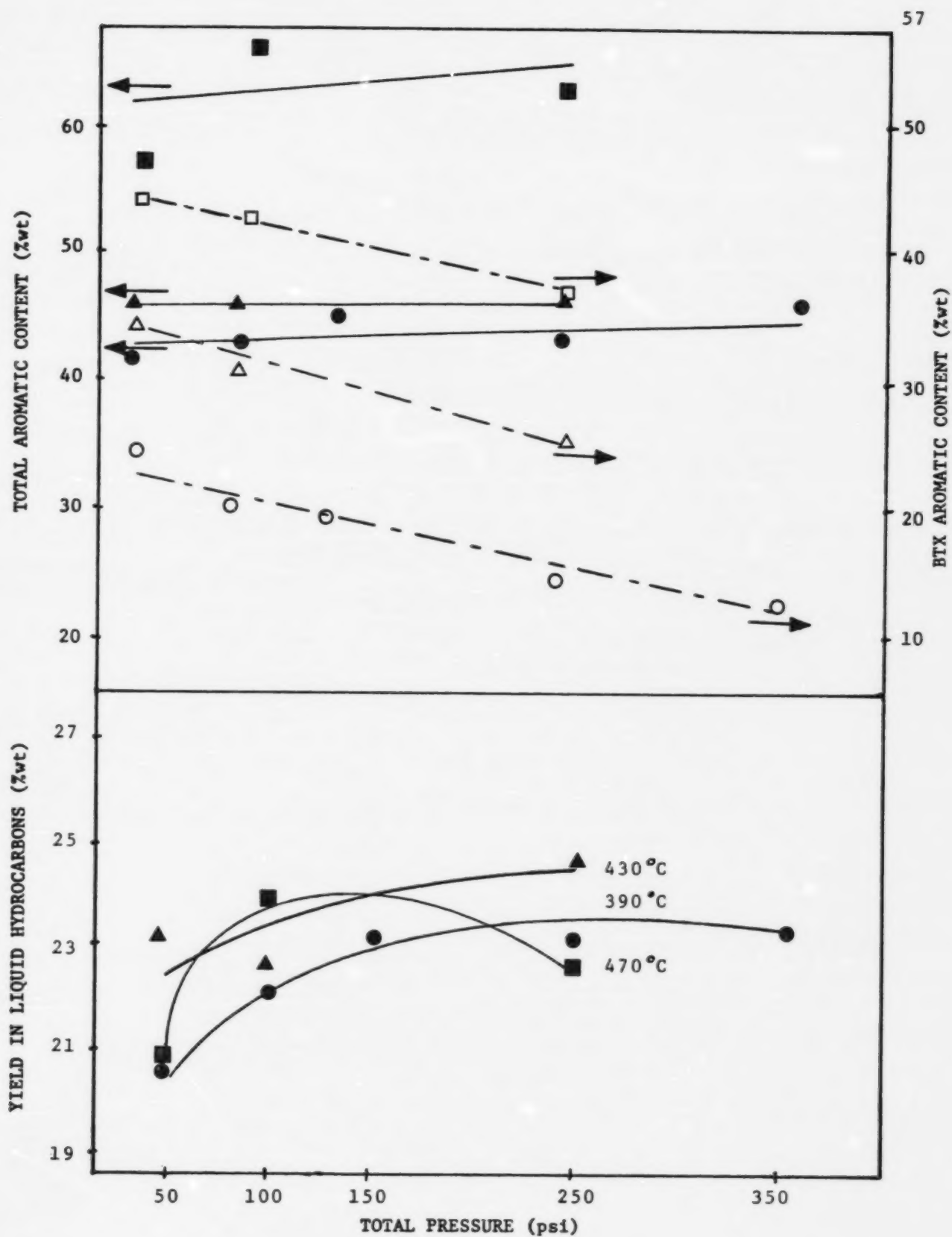


FIGURE: 6 CATALYTIC BEHAVIOR OF HA-CAN 12/Zn WITH PURE MWTANOL

FIGURE: 7 CATALYTIC BEHAVIOR OF HP-CAN 10 with n-BUTANOL

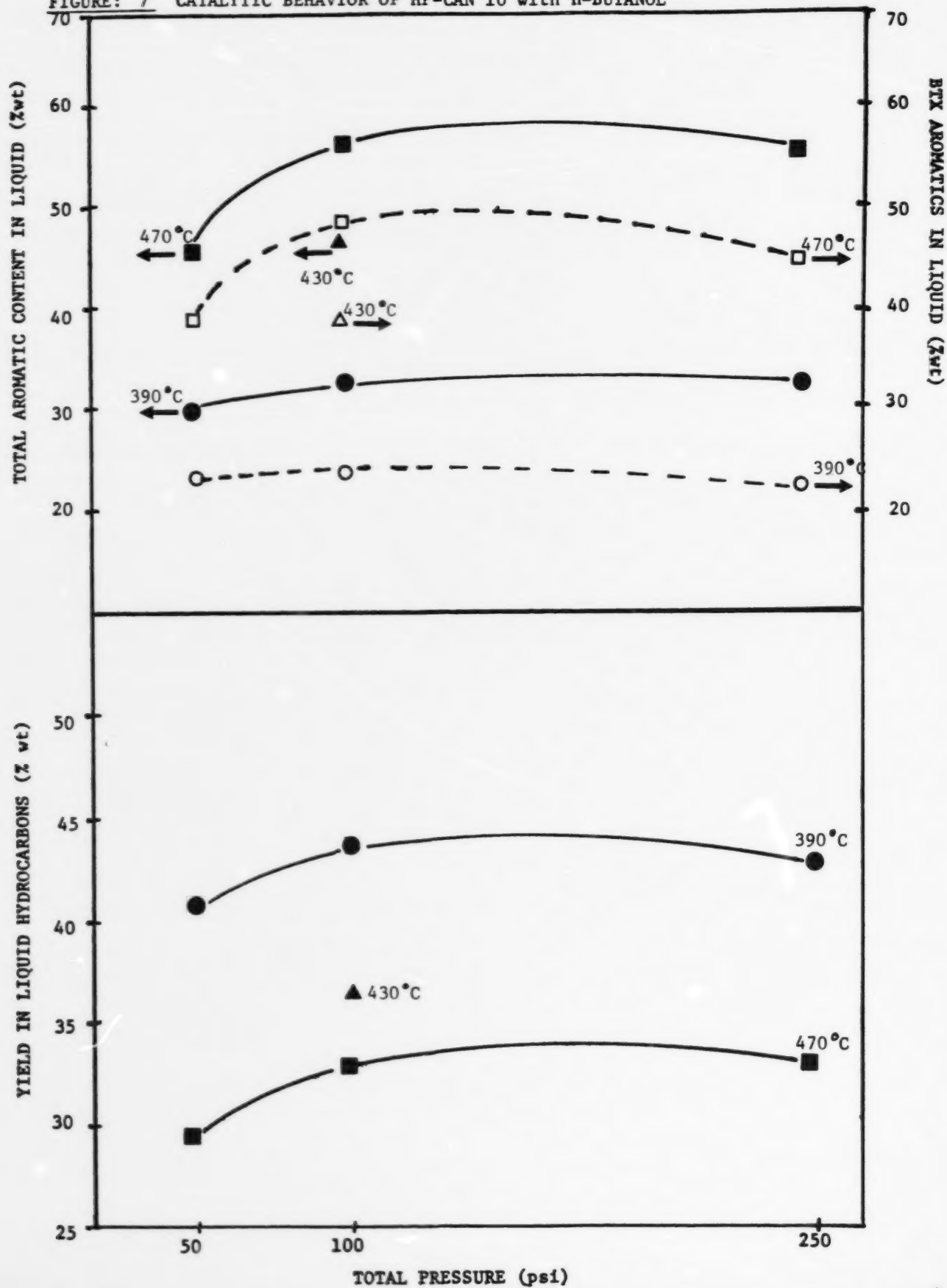


FIGURE: 8 CATALYTIC BEHAVIOR OF HP-CAN 10/Zn with n-BUTANOL

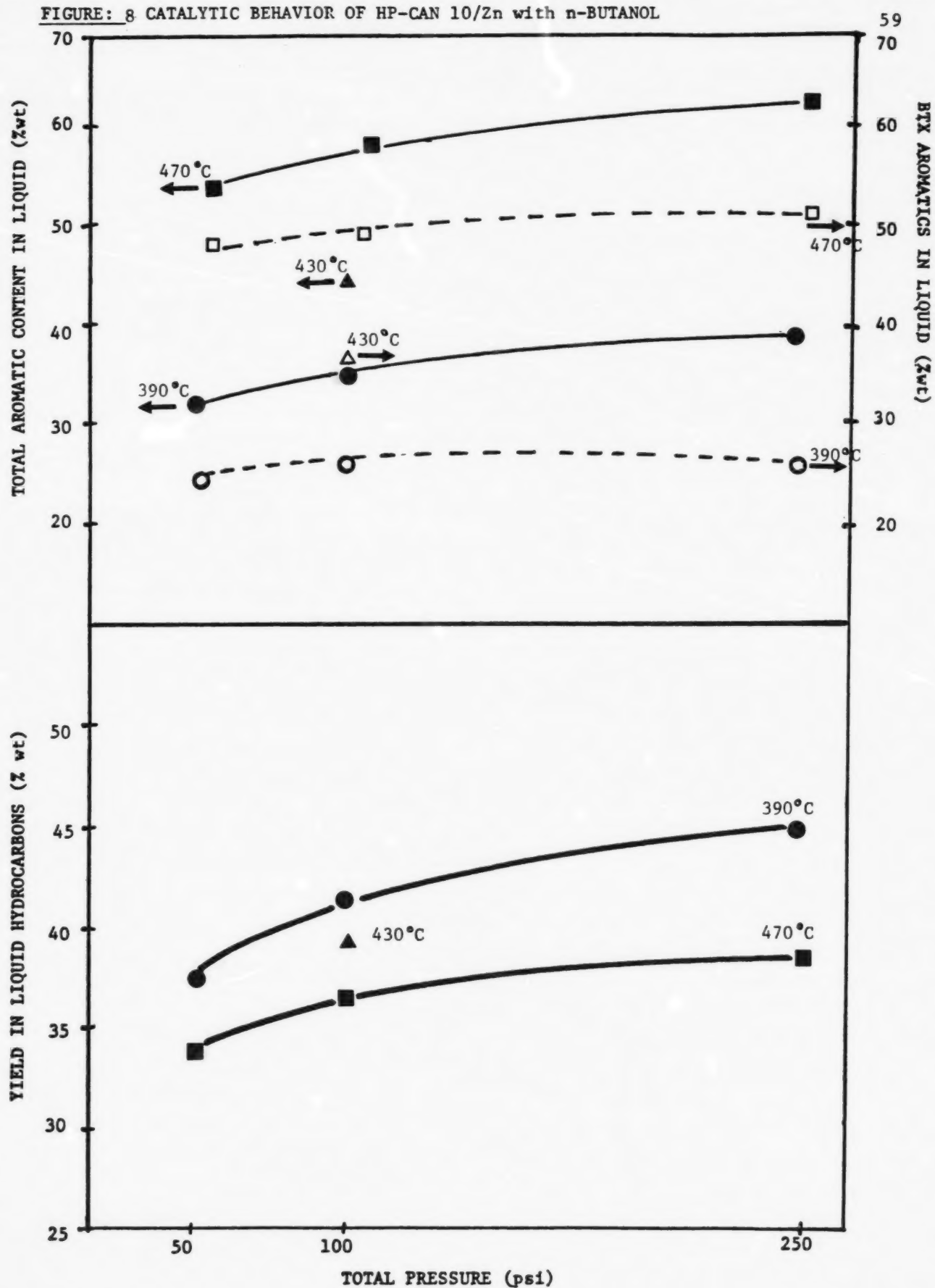
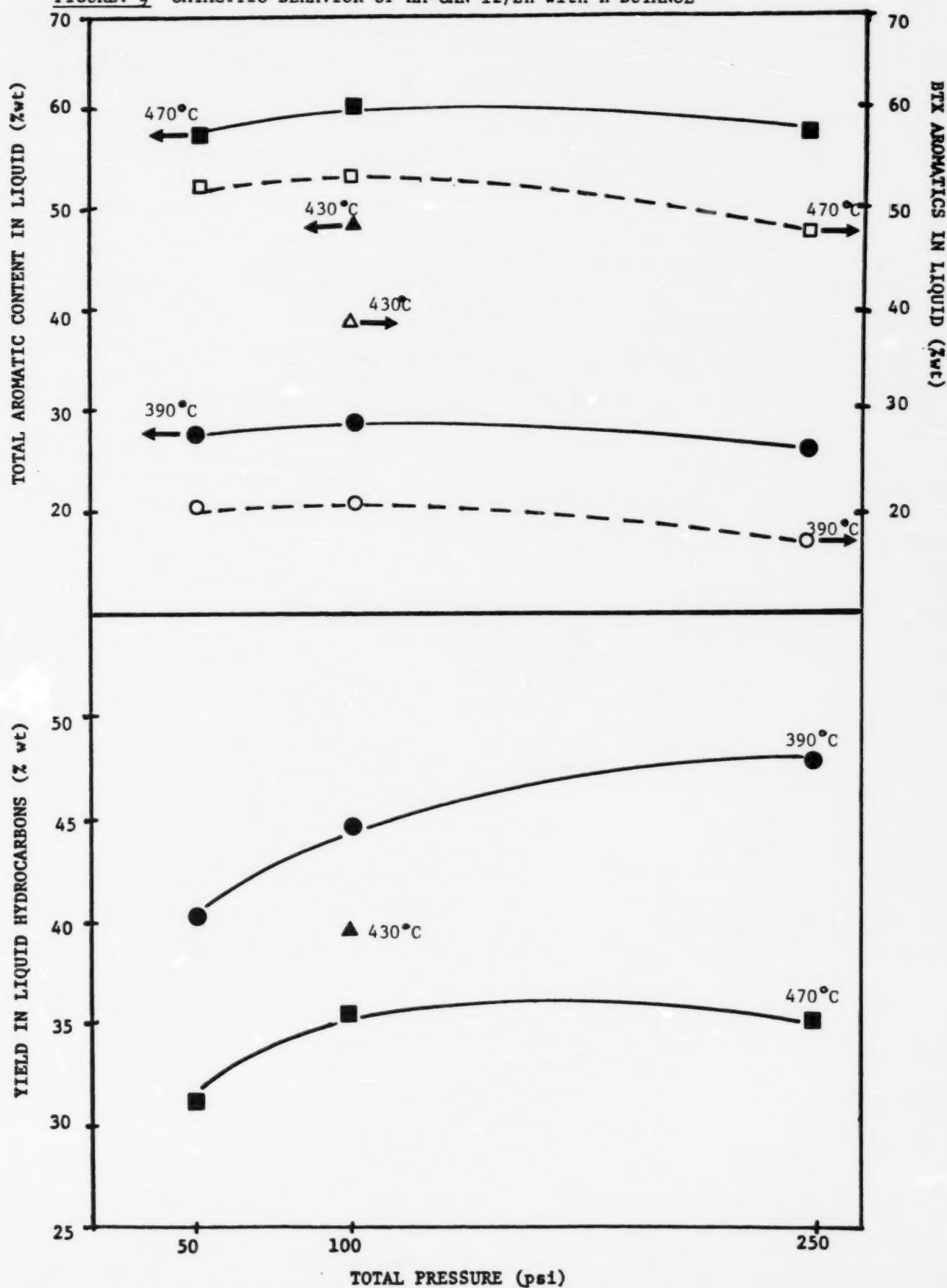
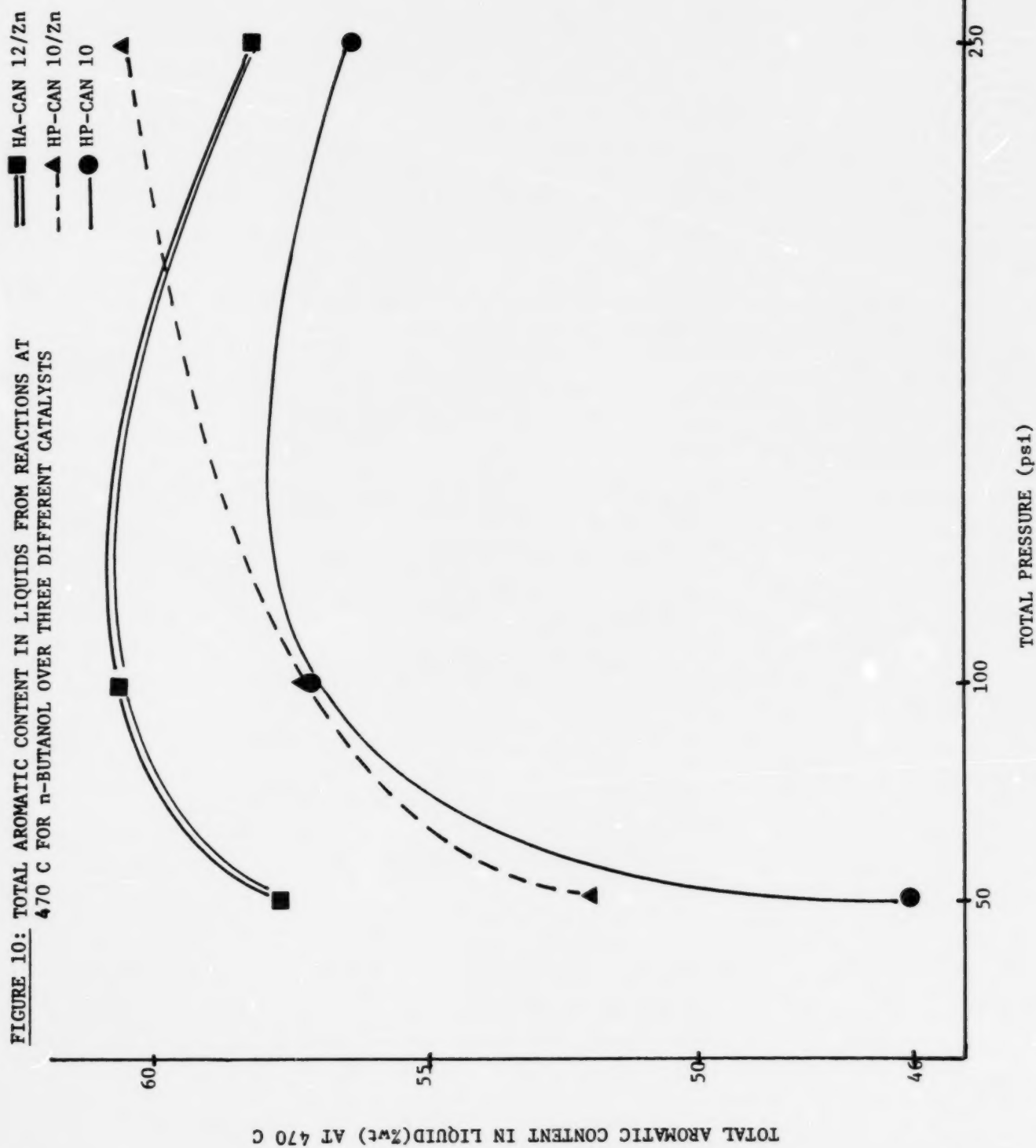


FIGURE: 9 CATALYTIC BEHAVIOR OF HA-CAN 12/Zn with n-BUTANOL





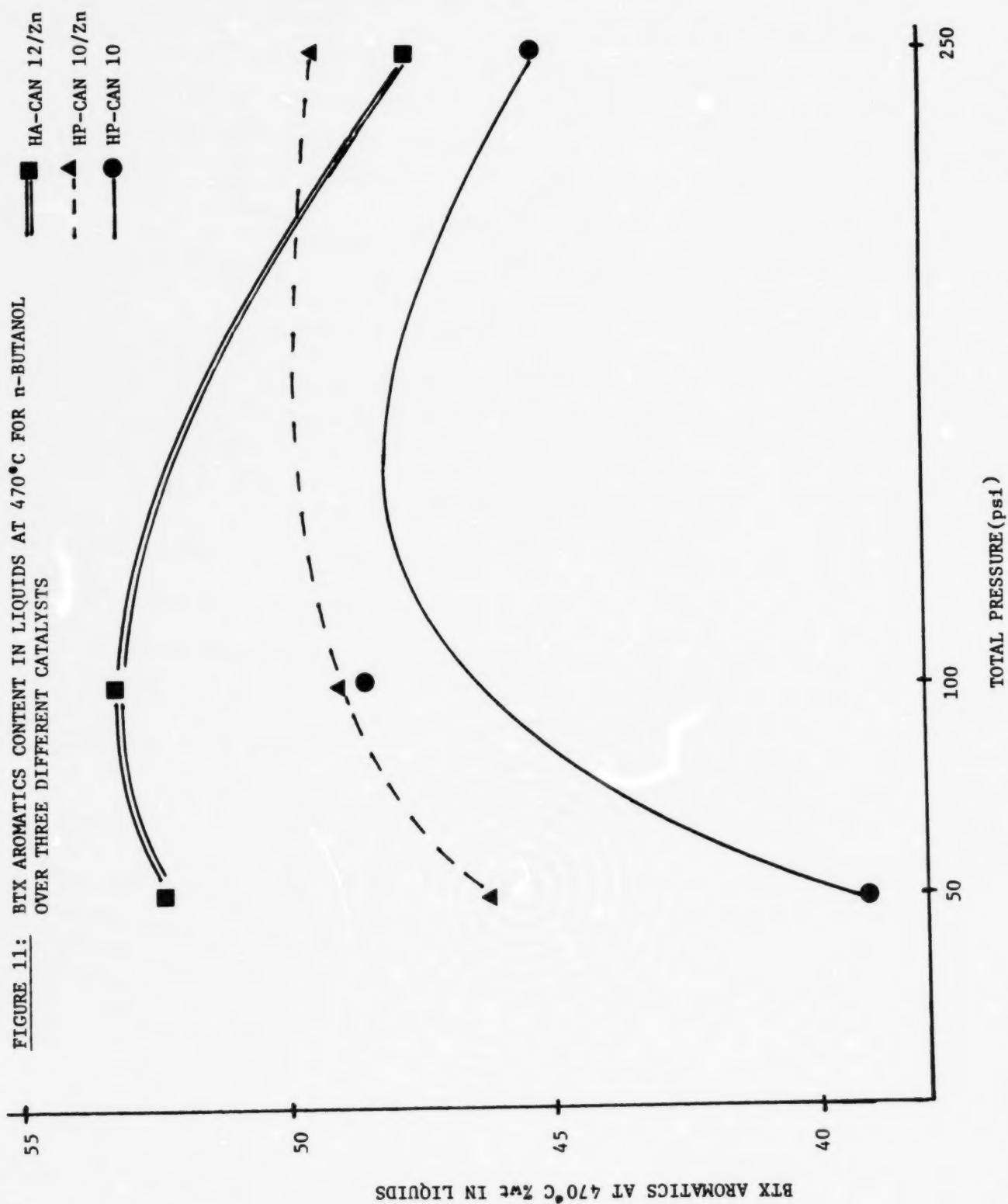


FIGURE: 12 CATALYTIC BEHAVIOR OF HP-CAN 10 with Iso-BUTANOL

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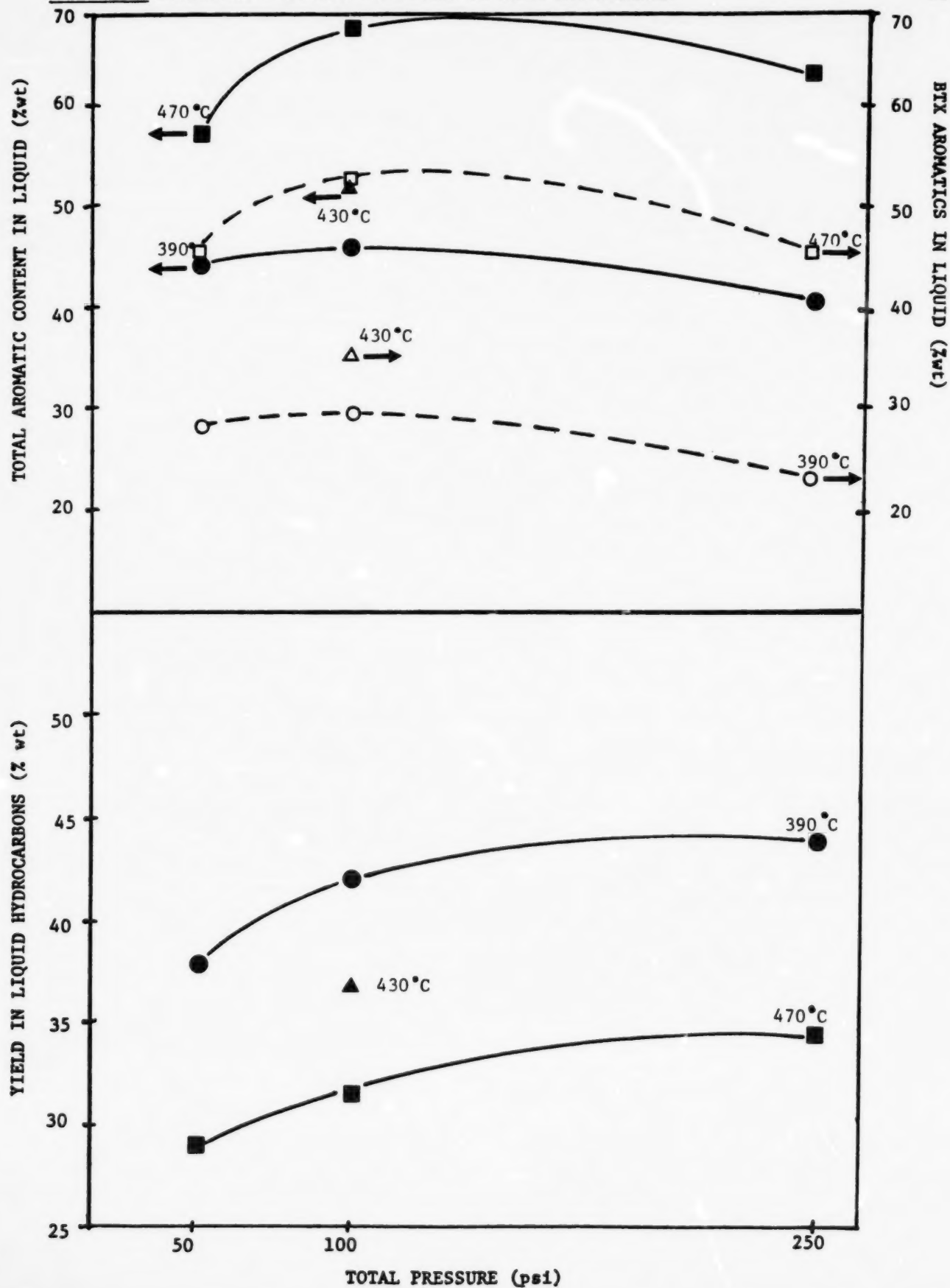


FIGURE:13 CATALYTIC BEHAVIOR OF HP-CAN 10/Zn with Iso-BUTANOL

64

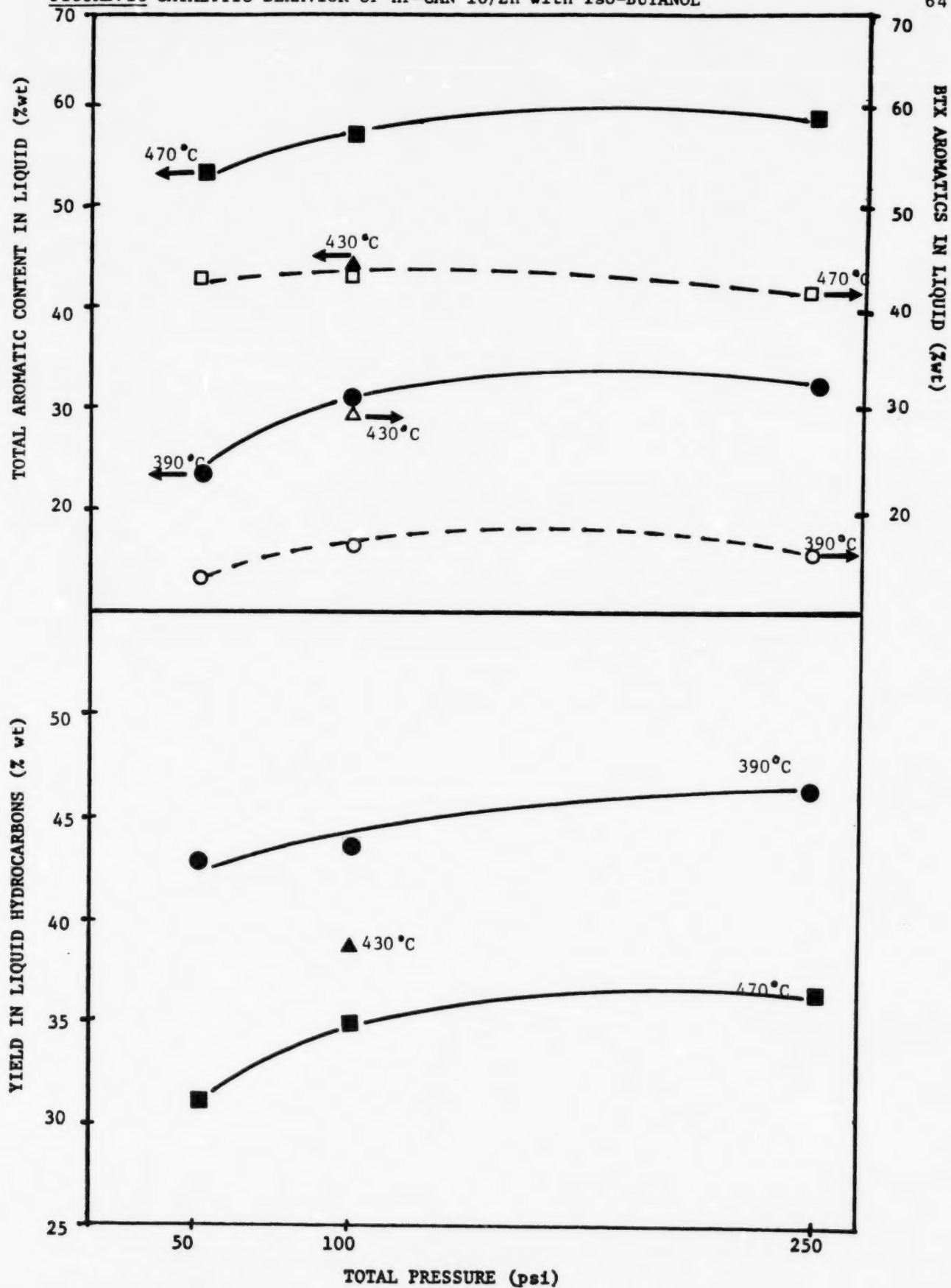
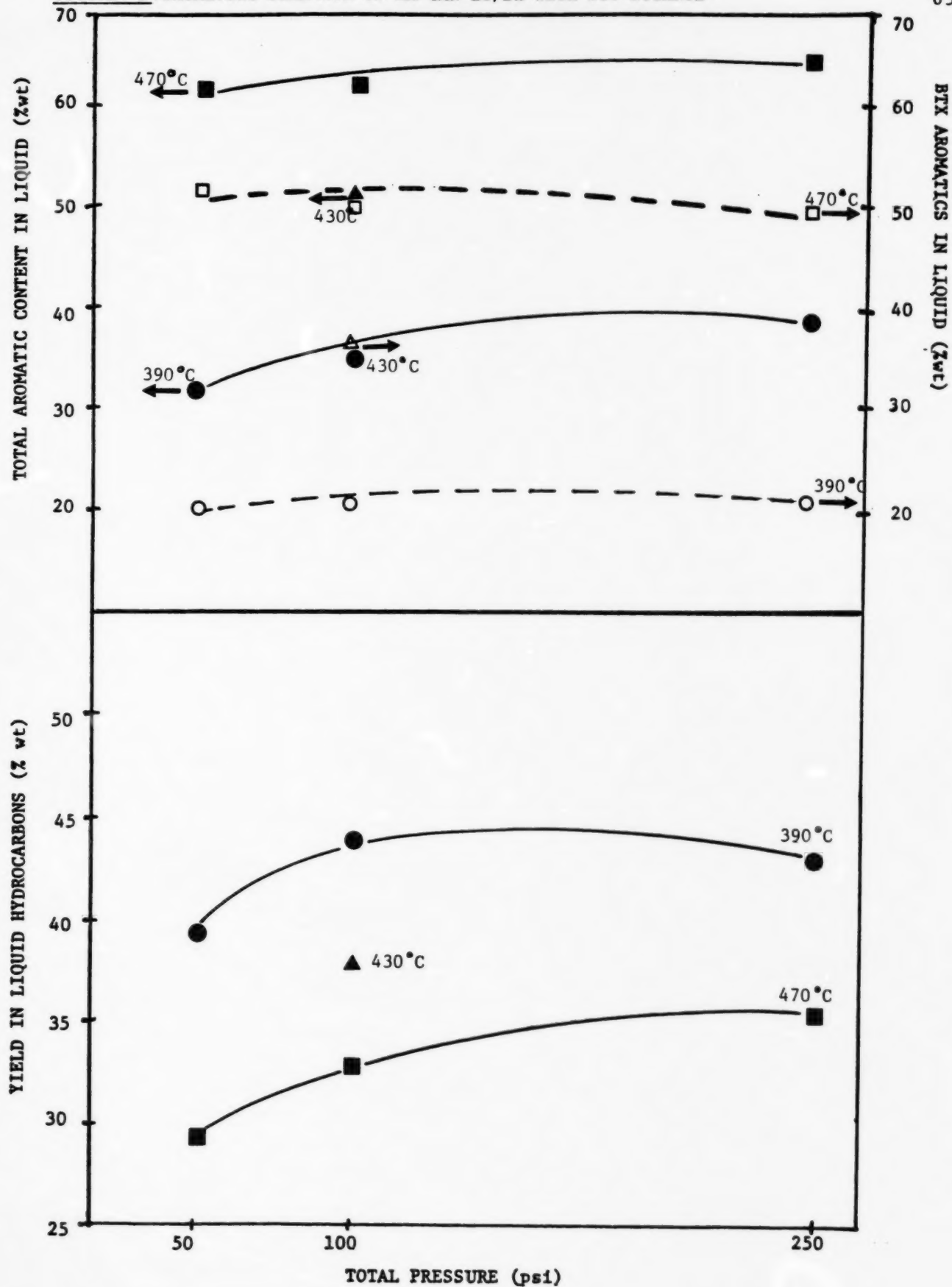
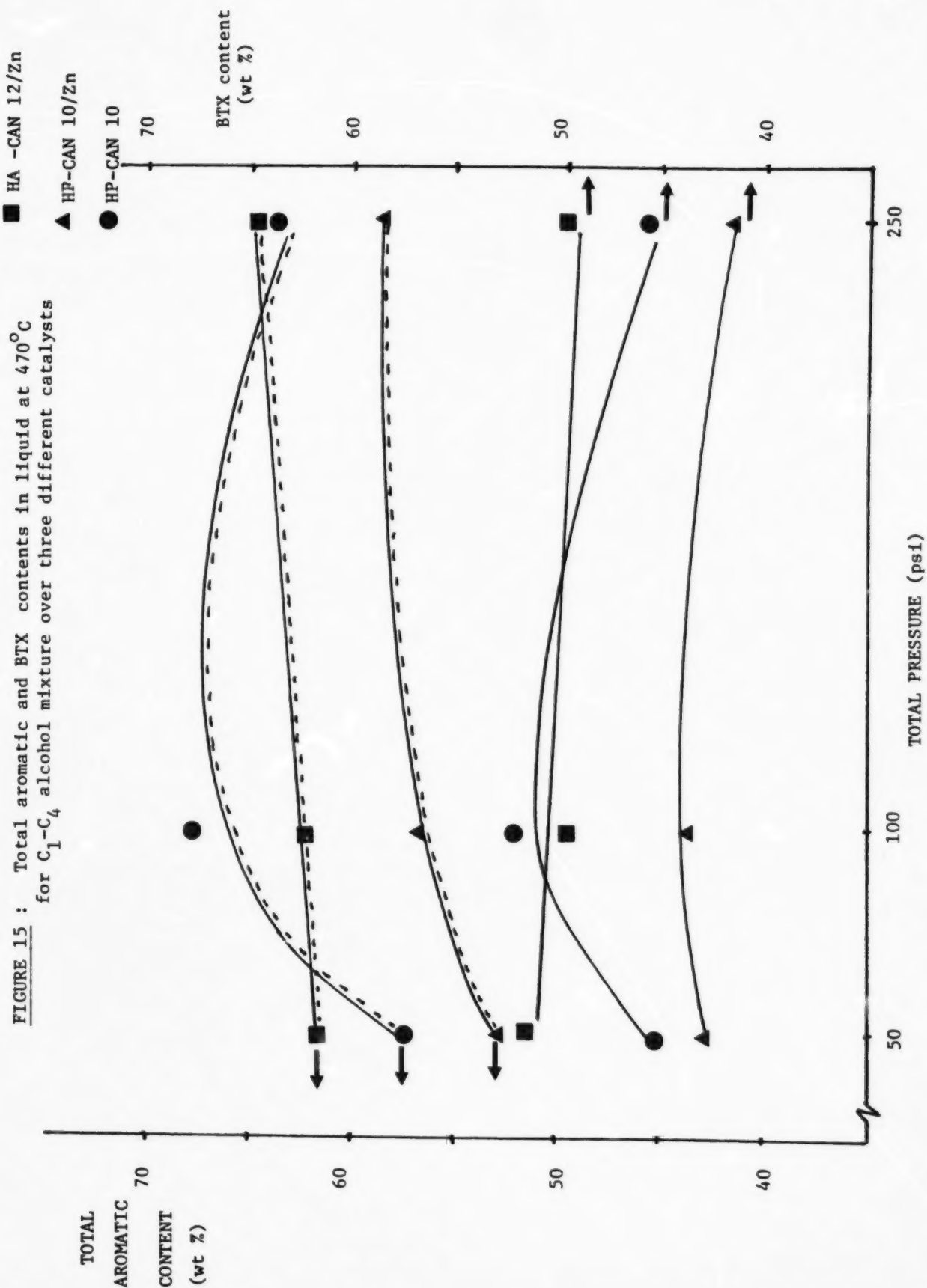


FIGURE: 14 CATALYTIC BEHAVIOR OF HA-CAN 12/Zn with Iso-BUTANOL

65





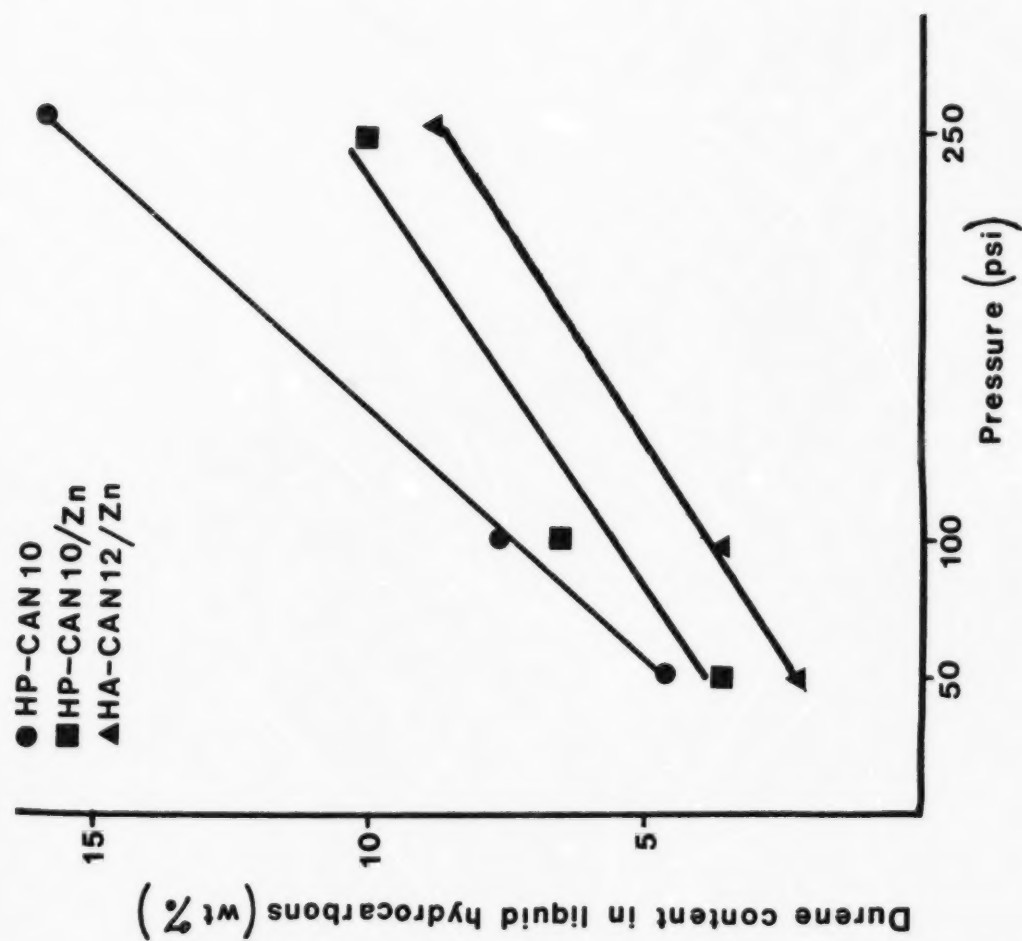


FIGURE 16 DURENE CONTENT IN LIQUID HYDROCARBONS AT $T=390^{\circ}\text{C}$

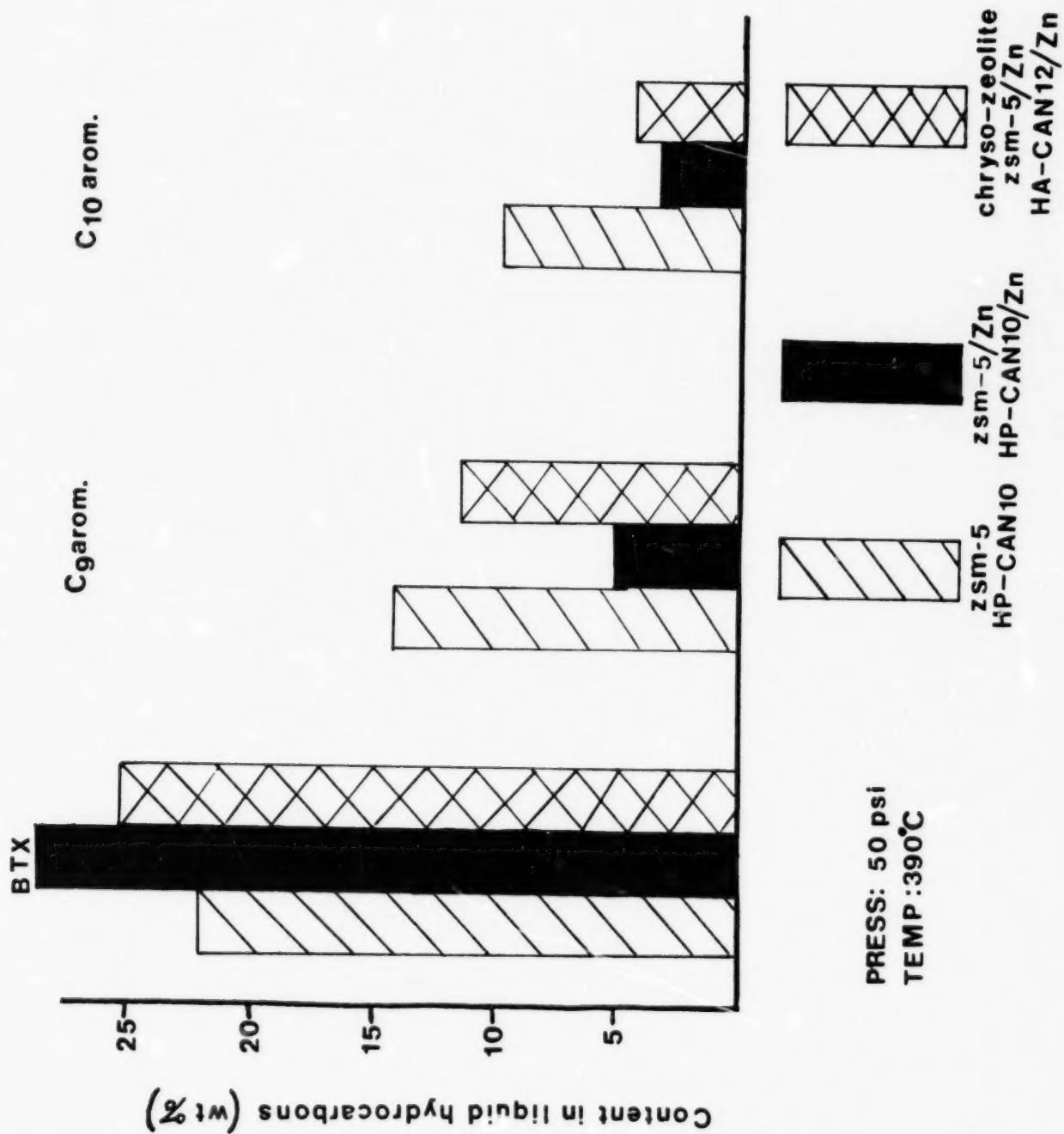


FIGURE 17 AROMATIC PRODUCT DISTRIBUTION AT T=390°C, PRESSURE= 50 p.s.i.

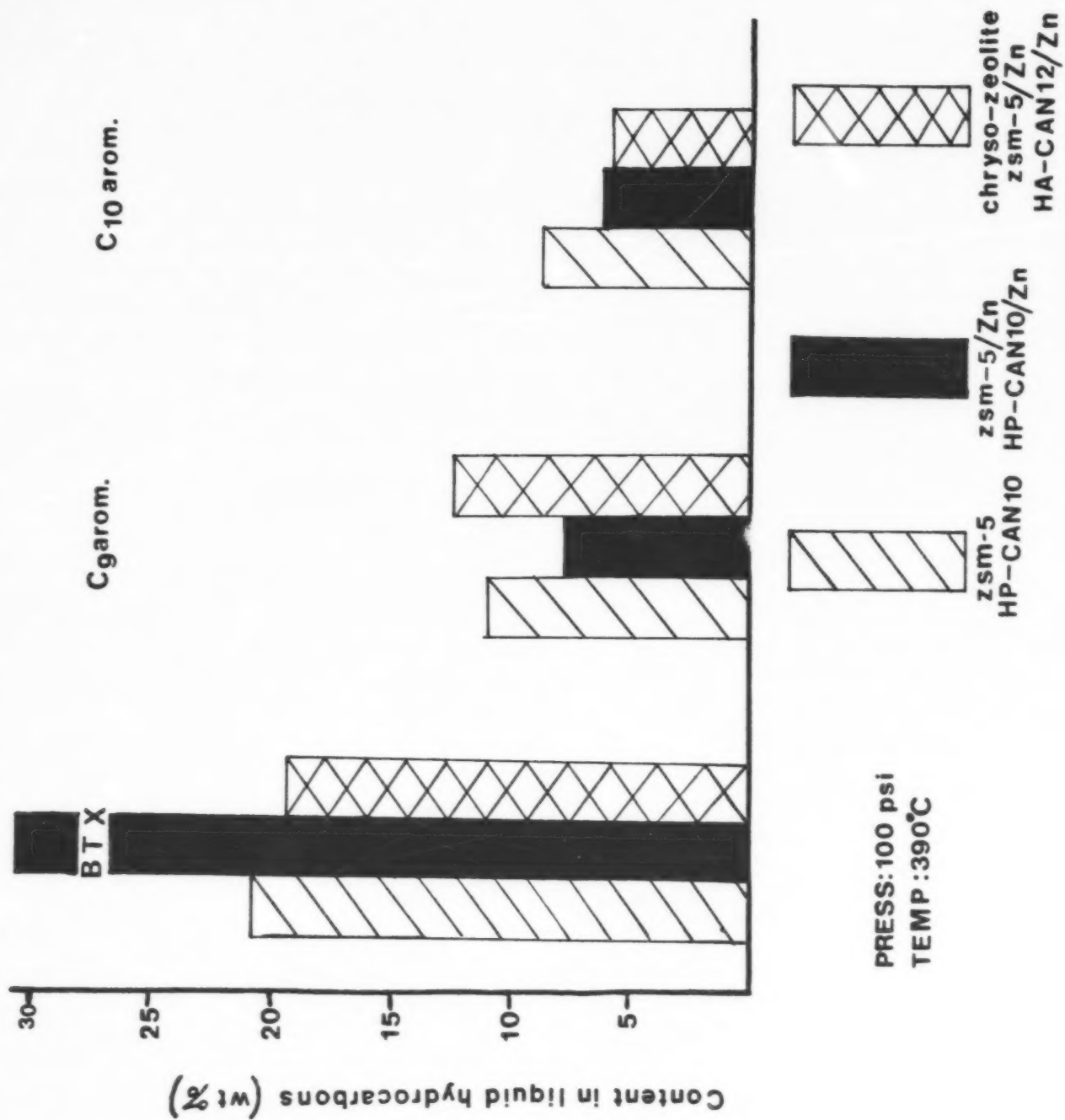


FIGURE 18 AROMATIC PRODUCT DISTRIBUTION AT T=390°C, PRESSURE=100 p.s.i.

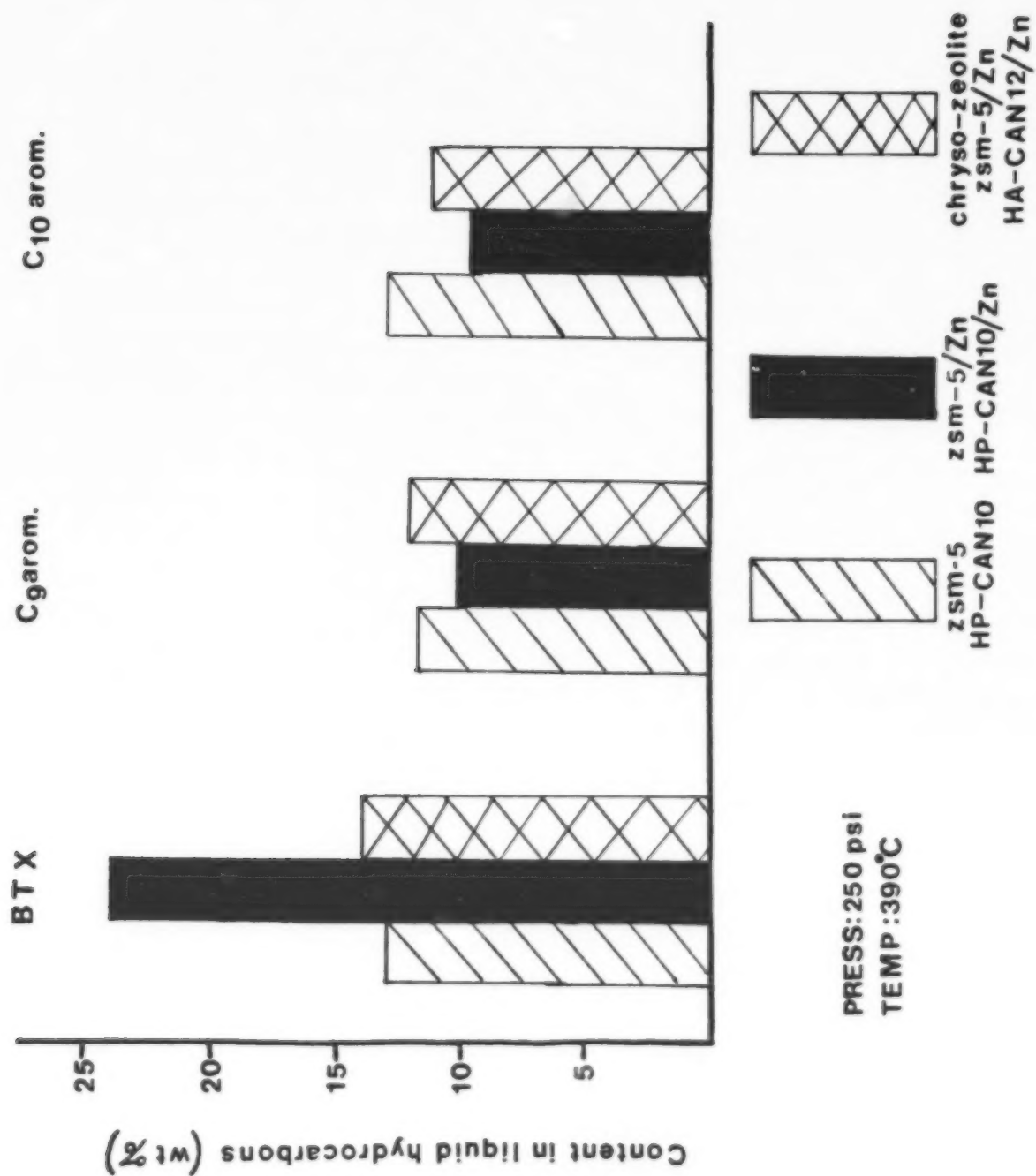


FIGURE 19 AROMATIC PRODUCT DISTRIBUTION AT T=390°C, PRESSURE=250 p.s.i.

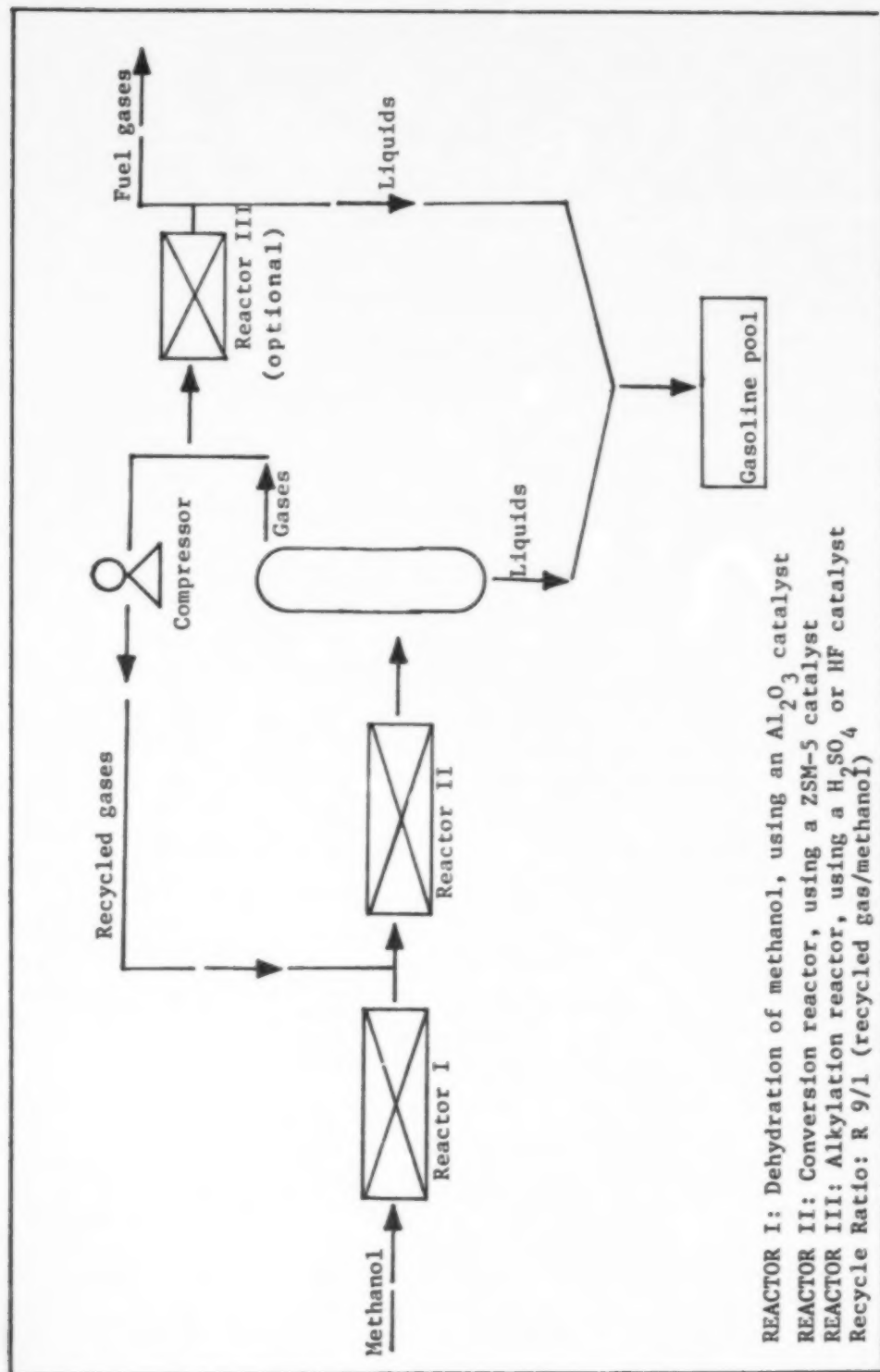


FIGURE of the Methanol-to-Gasoline (MTG) Process (fixed bed technology)